

PREDICTING SOOTING TENDENCY OF OXYGENATED FUEL USING MACHINE LEARNING

BY

MOHAMMED AMEEN AHMED QASEM

A Dissertation Presented to the
COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

In

CHEMICAL ENGINEERING

JANUARY 2024

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **MOHAMMED AMEEN AHMED QASEM** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING.**



Dr. Hassan M. Baaqeel
Department Chairman



Dr. Suliman Saleh Al-Homidan
Dean of Graduate Studies

Date _____



Dr. Eid Mussad Al-Mutairi
(Advisor)



Dr. Abdul Gani Abdul Jameel
(Co-Advisor)



Dr. Sagheer Onaizi
(Member)



Dr. Shaikh Abdur Razzak
(Member)



Dr. Basheer Chanbasha
(Member)



© Mohammed Ameen Ahmed Qasem

2024

[This work is dedicated to everyone who has supported me throughout my life, especially
my parents, siblings, wife, and children.]

ACKNOWLEDGMENTS

I want to start by deeply appreciating Allah, the Almighty, for providing me with the ability to effectively complete my thesis. I am particularly thankful to my advisor, Dr. Eid Mussad Al-Mutairi, for his ongoing encouragement during every difficult situation I faced while focusing on my thesis. Furthermore, I am especially grateful for the support and guidance of my co-advisor, Dr. Abdul Gani Abdul Jameel, who has always been available to listen, respond to my questions, review my report, and offer insightful feedback.

I would also like to express my gratitude to Drs. Sagheer Onaizi, Shaikh Abdur Razzak, and Basheer Chanbasha, who served on my thesis committee, for their helpful comments and advice throughout the writing of my thesis. I am extremely grateful to my parents, siblings, wife, and children for their ongoing support. I particularly want to acknowledge my parents, who have been a constant source of inspiration with their interest, confidence, and patience.

Moreover, I am deeply thankful to King Fahd University of Petroleum and Minerals (KFUPM) for granting me the opportunity to further my graduate studies. Additionally, I would like to extend my sincere thanks to KFUPM's Chemical Engineering Department for their great assistance.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES.....	VIII
LIST OF FIGURES.....	X
LIST OF ABBREVIATIONS.....	XV
ABSTRACT	XVI
ملخص الرسالة	XVIII
CHAPTER 1: INTRODUCTION	1
1.1 Thesis Motivation	1
1.2 Thesis Objectives	3
1.3 Methodology	4
CHAPTER 2: SMOKE POINT PREDICTION OF OXYGENATED FUELS USING NEURAL NETWORKS.	6
2.1 Experimental Section	10
2.1.1 Materials	11
2.1.2. Experimental procedure for SP measurement.....	11
2.1.3 ¹ H NMR spectroscopy.....	12
2.2 METHODOLOGIES	13
2.2.1 Dataset	13
2.2.2 Determination of the functional groups	41
2.2.3 ANN development.....	43
2.3 Results and Discussions.....	46
2.3.1 Paraffinic CH ₃ groups	46
2.3.2 Paraffinic CH ₂ groups	48
2.3.3 Paraffinic CH groups.....	50
2.3.4 Olefinic –CH=CH ₂ groups	51

2.3.5 Naphthenic –CH–CH ₂ groups	52
2.3.6 Aromatic C–CH groups	53
2.3.7 Alcoholic OH groups.....	55
2.3.8 Ether O groups	56
2.3.9 Molecular weight	58
2.3.10 Branching index (BI).....	59
2.3.11 ANN model.....	61
2.4 Conclusions	62

CHAPTER 3: A MACHINE LEARNING MODEL FOR PREDICTING THRESHOLD SOOTING INDEX (TSI) OF FUELS CONTAINING ALCOHOLS AND ETHERS. 64

3.1 METHODOLOGY	68
3.1.1 Dataset	68
3.1.2 Computing the functional groups.....	92
3.1.3 ANN development	96
3.2 Results & Discussions	98
3.2.1 Paraffinic CH ₃ groups.....	98
3.2.2 Paraffinic CH ₂ groups.....	Error! Bookmark not defined.
3.2.3 Paraffinic CH groups	101
3.2.4 Olefinic -CH=CH ₂ groups	102
3.2.5 Naphthenic -CH-CH ₂ groups.....	103
3.2.6 Aromatic C-CH groups.....	104
3.2.7 Alcoholic OH groups.....	105
3.2.8 Ether O groups	107
3.2.9 Molecular weight	108
3.2.10 Branching index (BI).....	109
3.2.11 Final ANN Model.....	110
3.3 Conclusion.....	114

CHAPTER 4: SOOTING PROPENSITY TRENDS FOR DIESEL/GASOLINE-ETHER BLENDS AND THEIR PREDICTION USING ANN. 116

4.1 EXPERIMENTAL WORK	120
4.1.1 Chemicals	120
4.1.2 Fuels	120
4.1.3 Approach.....	121
4.2 Results and discussions	121
4.2.1 Model constants	121
4.2.2 Sooting Indices for Diesel/Gasoline-Oxygenates Blends.....	122
4.2.3 Blending the base fuel and oxygenates.	126

4.3 Aromatics' effect.....	136
4.4 PREDTION of SP, TSI and OESi using ANN.	140
4.4.1 Methodologies	140
4.5 Conclusion	152
 CHAPTER 5: CHARACTERIZATION OF SOOT EMITTED FROM THE ATMOSPHERIC COMBUSTION OF DIETHYL ETHER-DIESEL BLENDS.	 154
5.1 Experimental.....	157
5.1.1 Materials	157
5.1.2 Methodologies	157
5.2 Results and discussion	159
5.2.1 Scanning electron microscopy (SEM)	159
5.2.2 Low/high resolutions of transition electron microscopy (LR/HR-TEM)	160
5.2.3 CHNS analyzer and Energy-dispersive X-ray spectroscopy (EDS/EDX)	163
5.2.4 X-ray diffraction (XRD)	165
5.2.5 Raman spectroscopy	167
5.2.6 Proton nuclear magnetic resonance (¹ H-NMR) spectroscopy	169
5.2.7 Thermogravimetric (TGA) analysis	173
5.3 Conclusion	176
 CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS	 178
 REFERENCES.....	 180
 APPENDIX.....	 196
1. SP model:.....	196
2. TSI model:	200
3. OESi model:	205
 VITAE	 212

LIST OF TABLES

Table 1: SP of pure compounds	14
Table 2: SP of mixtures.....	21
Table 3: Optimized hyperparameters of the final model	61
Table 4 :TSI of pure compounds	69
Table 5: TSI of surrogate mixtures	76
Table 6: Range of hyper-parameters employed.....	98
Table 7: The optimized hyper-parameters of the ANN model	111
Table 8: Chemical structures of tested compounds	116
Table 9: Properties of tested compounds	120
Table 10: Functional groups and Branched Index (BI) of fossil and oxygenated (pure and blends) fuels.....	127
Table 11: SP, TSI, and OESi of mixtures	140
Table 12: Optimized hyperparameters of the final SP model.....	148
Table 13: Optimized hyperparameters of the final TSI model	150
Table 14: Optimized hyperparameters of the final OESi model.....	151
Table 15: The combustion products from diethyl ether blend soot using a Vario MICRO cube CHNS analyzer.....	164
Table 16: ¹ H-NMR functional groups and chimerical shift for DEE5D (5 vol% diethyl ether and 95 vol% diesel) and DEE20D (20 vol% diethyl ether and 80 vol% diesel) soot	172

LIST OF FIGURES

Figure 1: Schematic of an artificial neural network (ANN).	10
Figure 2: SP measurement of fuel blend consisting of diphenyl ether (20%) and diesel (80%) by volume.	12
Figure 3: 1H-NMR spectra of gasoline and diesel samples.....	13
Figure 4: Functional group distribution of some pure compounds: (a) n-butane, (b) 1-hexene, (c) ethyl cyclohexane, (d) propyl benzene, (e) 2-methyl 1-butanol, and (f) diethylene glycol methyl ether.	42
Figure 5: Functional group distribution of sample blends. Compositions are expressed in vol% (a) 70% n-heptane–30% toluene, (b) 33.3% toluene–33.3% iso-octane–33.3% n-heptane, and (c) 70% TPGME (tripropylene glycol methyl ether) –30% TMB (1,2,4-trimethylbenzene), (d) 20% diethyl ether–80% gasoline (Vol%), (e) 10% tetralin –31.5 heptane–58.5 toluene, and (f) 70% 1-butanol – 30% 1,2,4 trimethylbenzene.	43
Figure 6: Input and output features are represented using Pearson’s correlation.	45
Figure 7: Effect of paraffinic CH ₃ groups on SPs of (a) pure compounds and (b) blends (iso-octane–toluene (A); HMN–TMB (B); m-xylene–n-dodecane (C); MCH–1-MN (D); TMB–1-MN (E); n-heptane–toluene (F); naphthalene– n-heptane–toluene (G); n-octane–n-heptane–toluene (H); HD–TMB (I); TPGME–TMB (J); diphenyl ether–gasoline (K); methyl tert-butyl ether (MTBE)– gasoline (L); diphenyl ether–diesel (M); diethyl ether–gasoline(N) and dibutyl ether–diesel (O)).	48
Figure 8: Effect of paraffinic CH ₂ groups on SPs of (a) pure compounds and (b) blends (iso-octane–toluene (A); HMN–TMB (B); m-xylene–n-dodecane (C); n-heptane–toluene (F); naphthene– n-heptane–toluene (G); n-octane–n-heptane–toluene(H); HD–TMB (I); TPGME–TMB (J); benzene–heptane–toluene(P); dioctyl ether–gasoline (Q); MTBE– gasoline (L); dibutyl ether–gasoline (R); diphenyl ether–diesel (M); diethyl ether–diesel (S) and dibutyl ether–diesel (O)).	50
Figure 9: Effect of paraffinic CH groups on SPs of (a) pure compounds and (b) blends (iso- .octane–toluene (A); HMN–TMB (B); diphenyl ether–gasoline (K); dioctyl ether–gasoline (Q); diethyl ether–gasoline (N); MTBE– gasoline (L); dibutyl ether–gasoline (R); diphenyl ether–diesel (M); diethyl ether–diesel (S); dibutyl ether–diesel (O) and TPGME–TMB (J))..	51
Figure 10: Effect of olefinic –CH=CH ₂ groups on SPs of (a) pure compounds and (b) blends (diphenyl ether–gasoline (K), dioctyl ether–gasoline (Q), diethyl ether–gasoline (N), MTBE– gasoline (L), and dibutyl ether–gasoline (R)).	52

Figure 11: Effect of naphthenic –CH–CH ₂ groups (wt%) on SPs of (a) pure compounds and (b) blends (MCH–1-MN (D), decalin-1-MN (T), tetralin-n-heptane-toluene (U), diphenyl ether–gasoline (K), dioctyl ether–gasoline (Q), diethyl ether–gasoline (N), MTBE– gasoline (L), dibutyl ether–gasoline (R), diphenyl ether–diesel (M), diethyl ether–diesel (S) and dibutyl ether–diesel (O))....	53
Figure 12: Effect of aromatic C–CH groups (wt%) on SPs of (a) pure compounds and (b) blends (iso-octane–toluene (A); HMN–TMB (B); m-xylene–dodecane (C); MCH–1-MN (D); TMB–1-MN (E); n-heptane–toluene (F); naphthene– n-heptane–toluene (G); n-octane–n-heptane–toluene (H); HD–TMB (I); TPGME–TMB (J); diphenyl ether–gasoline (K); diphenyl ether–diesel (M); dibutyl ether–diesel (O); benzene–n-heptane–toluene (P) and 1-MN–n-heptane–toluene (V)).	54
Figure 13: Effect of alcoholic OH groups (wt%) on SPs of (a) pure compounds and (b) blends (1-butanol–HD–TMB (W); TPGME–TMB (J); 1-undecanol–HD–TMB (X) and TPGME–HD–TMB (Y)).	56
Figure 14: Effect of ether O groups (wt%) on SPs of (a) pure compounds and (b) blends (diphenyl ether–gasoline (K); dioctyl ether–gasoline (Q); diethyl ether–gasoline (N); MTBE–gasoline (L); dibutyl ether–gasoline (R); diphenyl ether–diesel (M); diethyl ether–diesel (S); dibutyl ether–diesel (O); TPGME–TMB (J) and TPGME–HD–TMB (Y)).	58
Figure 15: Effect of MW on SPs of (a) pure compounds and (b) blends (iso-octane–toluene (A); HMN–TMB (B); m-xylene–dodecane (C); MCH–1-MN (D); TMB–1-MN (E); n-heptane–toluene (F); naphthalene–n-heptane–toluene (G); n-octane–n-heptane–toluene (H); HD–TMB (I); TPGME–TMB (J); diphenyl ether–gasoline (K); MTBE– gasoline (L); diphenyl ether–diesel (M); diethyl ether–diesel (S) and dibutyl ether–diesel (O)).	59
Figure 16: Effect of BI on SPs of (a) pure compounds and (b) blends (iso-octane–toluene (A), HMN–TMB (B); m-xylene–dodecane (C); MCH–1-MN (D); TMB–1-MN (E); n-heptane–toluene (F); naphthene– n-heptane–toluene (G); n-octane–n-heptane–toluene (H); HD–TMB (I); TPGME–TMB (J); diphenyl ether–gasoline (K); MTBE– gasoline (L); diphenyl ether–diesel (M); diethyl ether–diesel (S) and dibutyl ether–diesel (O)).	60
Figure 17: Comparison between the predicted and measured SPs.	62
Figure 18: A schematic representation of an ANN.	68
Figure 19: Functional groups distribution of some pure compounds .	93
Figure 20: Functional group distribution of some fuel surrogate mixtures.	

The compositions in vol% are expressed as follows:

(A) 5% methylnaphthalene + 95% iso-octane, (B) Jet-A (47.06% n-dodecane + 16.69% iso-cetane + 24.19% decalin + 12.06% tol), (C) 11.5% TPGME + 38.5% NHD + 50% 1,2,4 TMB, (D) 43.5% UnOH + 26.5% NHD + 30% 1,2,4TMB, (E) 35% n-tetradecane + 35% decalin + 30% 1,3,5 TMB, (F) 23.5% TPGME + 26.5% NHD + 50% 1,2,4 TMB	94
Figure 21: The inputs and the output features represented by Pearson correlation.	97
Figure 22: Effect of paraffinic CH ₃ groups on TSI of (a) pure compounds; and (b) surrogate fuel mixtures.....	100
Figure 23: Effect of paraffinic CH ₂ groups on TSI of (a) pure compounds; and (b) surrogate fuel mixtures	101
Figure 24: Effect of paraffinic CH groups on TSI of (a) pure compounds; and (b) surrogate fuel mixtures.....	102
Figure 25: Effect of olefinic -CH=CH ₂ groups on TSI of pure compounds	103
Figure 26: Effect of naphthenic -CH-CH ₂ groups (wt %) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures.....	104
Figure 27: Effect of Aromatic C-CH groups (wt %) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures	105
Figure 28: Effect of alcoholic OH groups (wt %) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures.....	107
Figure 29: Effect of ethers O groups (wt %) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures.....	108
Figure 30: Effect of Molecular weight (g/mol) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures.....	109
Figure 31: Effect of branching index (BI) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures	110
Figure 32: Architecture of the ANN model developed for TSI prediction.....	111
Figure 33: Comparison between predicted and measured TSI values.....	112
Figure 34: Absolute error between the measured and the predicted TSI values.	114
Figure 35: TSI and OESI of 20 vol% oxygenates in 80 vol% diesel blends, including diethyl ether-diesel (DEE-D), dioctyl ether-diesel (DOE-D), diphenyl ether-diesel (DPE-D), dibutyl ether-diesel (DBE-D), and methyl tert butyl ether-diesel (MTBE-D), plotted against the oxygen content (wt%) and the molar ratio (O/C) of the oxygenates. Panels (a) and (c) display the TSI, while panels (b) and (d) show the OESI.	123

Figure 36: (a & c) TSI and (b & d) OESI of 20 vol% oxygenates-80 vol% diesel blends (diethyl ether-diesel (DEE-D), dioctyl ether-diesel (DOE-D), diphenyl ether-diesel (DPE-D), dibutyl ether -diesel (DBE-D)) and methyl tert butyl ether-diesel (MTBE-D)) vs. molar ratio(H/C) and boiling point of oxygenates.	124
Figure 37: The TSI (a and c) and OESI (b and d) of blends containing 20 vol% oxygenates (diethyl ether-diesel (DEE-D), dioctyl ether-diesel (DOE- D), diphenyl ether-diesel (DPE-D), dibutyl ether-diesel (DBE-D), and methyl tert-butyl ether-diesel (MTBE-D)), in relation to the density and molecular weight of the oxygenates.	126
Figure 38: Values of (a)TSI and (b) OESI for gasoline (91)-ethers blends.....	132
Figure 39: Values of (a)TSI and OESI(b) for Diesel -ethers blends.....	135
Figure 40: Input and output features represented using Pearson's correlation for SP model.	146
Figure 41: Input and output features represented using Pearson's correlation for TSI model.....	147
Figure 42: Input and output features represented using Pearson's correlation for OESI model.	148
Figure 43: Comparison between the predicted and measured SPs. ...	150
Figure 44: Comparison between the predicted and measured TSIs.....	151
Figure 45: Comparison between the predicted and measured OESIs..	152
Figure 46: Collection of the soot using the Al foil covering the smoke point lamp.....	158
Figure 47: Soot from the atmospheric combustion of diesel-oxygenates blend: (a and b) 95 vol% diesel 5vol% diethyl ether (DEE5D) and (c and d) 80 vol% diesel 20 diethyl ether (DEE20D)	161
Figure 48: HR-TEM images of soot obtained from the atmospheric combustion of diesel-diethyl-ether blend:(a and c) 5% vol diethyl ether and 95 % vol diesel (DEE5D) and (b and d): 20% vol diethyl ether and 80 vol% diesel (DEE20D)	163
Figure 49: Soot from the atmospheric combustion of diesel-diethyl ether blend has :(a) Percentage of the sulfur of (A) DEE5D and (B) DEE20D using CHNS analyzer; and (b) Spectra of Energy dispersive spectroscopy (EDS) of DEE5D	165
Figure 50: Raman (a) and X-ray diffraction (b) spectra of soot from the atmospheric combustion of diesel-diethyl ether blend (DEE5D: 5% Diethyl ether and 95% Diesel; and DEE20D: DEE5D: 20% Diethyl ether and 80% Diesel, v/v)	167

Figure 51: ¹ H-NMR spectra of soot from the blend of	
(a) DEE5D (5% diethyl ether and 95 %diesel v/v) and	
(b) DEE20D (20% diethyl ether and 80 %diesel v/v) blends	169
Figure 52:TGA curves of soot from Diethyl ether -Diesel blend	
(DEE5D: 5% Diethyl ether and 95% Diesel;	
and DEE20D: DEE5D: 20% Diethyl ether and 80% Diesel, v/v)	
(a) under N2 atmosphere and (b) air	173

LIST OF ABBREVIATIONS

SP	Smoke Point
TSI	Threshold sooting index
OESi	Oxygen Extended Sooting Index
ANN	Artificial neural network
XRD	X-Ray Diffraction
CHNS	Carbon, Hydrogen, Nitrogen and Sulfur
HR-TEM	High-Resolution Transmission Electron Microscope
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-Ray
TGA	Thermogravimetric Analysis
^1H -NMR	Proton Nuclear Magnetic Resonance Spectroscopy
ASTM D1322	Standard Test Method for Smoke Point of Kerosene and Aviation Turbine Fuel
CHNS Analyzer	A technique for determining the carbon, hydrogen, nitrogen, and sulfur.
DEE5D	5% diethyl ether and 95% diesel v/v
DEE20D	20% diethyl ether and 80% diesel v/v
EDS	Energy-Dispersive X-Ray Spectroscopy

ABSTRACT

Full Name : [Mohammed Ameen Ahmed Qasem]

Thesis Title : [Predicting Sooting Tendency of Oxygenated Fuel Using Machine Learning]

Major Field : [Chemical Engineering]

Date of Degree : [January,2024]

Designing target fuels for specific combustion applications requires understanding various fuel properties, including sooting tendency indices such as Smoke Point (SP), Threshold Sooting Index (TSI), and Oxygen Extended Sooting Index (OESI), as well as physical, thermochemical, and combustion properties. Sooting tendencies are particularly crucial, given their significant environmental and health impacts. This study focuses on investigating the sooting tendency of oxygenated fuels. However, experimental measurement of sooting tendency is often challenging due to safety concerns or handling complexities of certain fuels. Moreover, accurate measurement demands costly and time-consuming instrumentation and skilled technicians.

Hence, there's a need for novel or enhanced approaches integrating mathematical models to predict fuel sooting tendency, thus reducing experimental measurement costs and time. In this context, we measured the smoke points of various oxygenated fuels using an SP lamp apparatus. Subsequently, we employed functional groups and machine learning tools such as Artificial Neural Networks (ANNs) to develop innovative models establishing mathematical relationships between fuel sooting tendency and composition.

Functional groups were identified and quantified using techniques like Nuclear Magnetic Spectroscopy ($^1\text{H-NMR}$) to summarize fuel molecular information. These groups, along with features representing molecular structure (branching and molecular weight), were utilized to predict oxygenated fuel sooting tendencies. ANNs were utilized to develop models predicting SP, TSI, and

OESI of oxygenated fuels, incorporating one output (SP, TSI, or OESI) and ten inputs (paraffinic CH₃, paraffinic CH₂, paraffinic CH, naphthenic CH-CH₂, olefinic -CH=CH₂, aromatic C-CH, alcohol OH, ether O groups, molecular weight, and branching index). Additionally, density and ratios of oxygen to carbon and hydrogen to carbon were sometimes considered.

The results demonstrated strong correlations between measured and predicted SP, TSI, and OESI, with values of 98%, 97%, and 96%, respectively. In conclusion, these models effectively predict oxygenated fuel sooting tendencies provided functional group information (paraffinic CH₃, paraffinic CH₂, paraffinic CH, naphthenic CH-CH₂, olefinic -CH=CH₂, aromatic C-CH, alcohol OH, and ether O groups), along with molecular weight and branching index, are available. Additionally, density and ratios of oxygen to carbon and hydrogen to carbon should sometimes be known.

Finally, fuel-oxygenate blends were characterized using various analytical techniques, including Carbon, Hydrogen, Nitrogen, and Sulfur (CHNS) analysis, spectroscopic techniques (Energy Dispersive X-Ray (EDX), Scanning Electron Microscopy (SEM), High-Resolution Transmission Electron Microscopy (HR-TEM), RAMAN spectrometry, Thermogravimetric Analysis (TGA), and nuclear magnetic resonance (NMR)), and X-ray diffraction (XRD). |

ملخص الرسالة

الاسم الكامل: محمد أمين أحمد قاسم

عنوان الرسالة: التنبؤ في مدى ميول سخام الوقود المؤكسج (المحتوي على الأكسجين) باستخدام التعلم الآلي

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: يناير/ 2024

يتطلب تصميم الوقود المستهدف لتطبيقات احتراق محددة معرفة خصائص الوقود ، مثل مؤشرات اتجاه السخام على سبيل المثال : نقطة دخان (SP) ، ومؤشر إطلاق العتبة (TSI) ، ومؤشر الأكسجين الممتد (OESi). تُستخدم الخصائص الفيزيائية (مثل: الكثافة واللزوجة) ، والخصائص الحرارية الكيميائية (على سبيل المثال: نقطة الوميض وحرارة الاحتراق) ، وخصائص الاحتراق لدراسة ميلان الوقود نحو انتاج السخام . ومع ذلك ، في هذا العمل تمت فقط مناقشة مؤشرات اتجاه السخام (SP و TSI و OES) وذلك بسبب أن هذه المؤشرات تؤثر بشكل كبير على صحة الإنسان والبيئة. وبالنسبة لقياساتها يمكن معرفتها عن طريق معرفة كم مدى ميول الوقود اتجاه السخام بتحديد نقطة دخان الوقود. ومع ذلك ، فمن الصعب أو من المستحيل في بعض الأحيان إجراء قياس تجريبي لجميع خصائص الوقود المستهدف ؛ لأن بعضها يشكل خطورة على صحة الإنسان أو يصعب التعامل معه. علاوة على ذلك ، يتطلب القياس التجريبي الدقيق لخصائص الوقود أجهزة متطورة وفنيين ذوي خبرة ، وهي مكلفة وتستغرق وقتاً طويلاً. لذلك ، هناك حاجة لتطوير مناهج جديدة أو محسنة تتضمن نماذج رياضية للتنبؤ بخصائص الوقود ، وبالتالي تقليل تكلفة وقت القياس التجريبي.

نظراً لأن هذه القياسات يتم إجراؤها في ظل الظروف والأدوات القياسية ؛ فإن القيم المقاسة توفر معلومات حول طبيعة الوقود يمكنها أن تساعد في توقع خصائص الوقود مثل الميول اتجاه السخام ، وذلك من خلال توصيف التركيبة الكيميائية للوقود باستخدام طرق معينة مثل المجموعات الوظيفية وأدوات التعلم الآلي . هناك الكثير من ادوات التعلم الآلي أو الذكاء الاصطناعي على سبيل المثال لا الحصر: الشبكات العصبونية الاصطناعية (ANNs) التي يمكن أن تستخدم في تطوير نماذج جديدة بحيث تنشئ علاقات رياضية بين خصائص الوقود وتركيباتها. وبما أن الوقود يتكون من جزيئات مختلفة تتكون من مجموعات وظيفية ؛ فإن هذه المجموعات يمكن استخدامها في تحديد خصائص الوقود مثل الميول في اتجاه السخام . يمكن تحديد هذه المجموعات وتحديد كميتها باستخدام تقنيات محددة مثل التحليل الطيفي المغناطيسي النووي (($^1\text{H-NMR}$) الذي يمكن أن يستخدم كطريقة لتحديد كميات المجموعات الوظيفية للوقود. لذلك هناك عشر صفات : ثمان مجموعات وظيفية (بارافيني CH_3 ، بارافيني CH_2 ، بارافيني CH ، نافثينيك CH-CH_2 ، أوليفيني CH=CH_2 ، عطري C-CH ، كحول OH ، ومجموعات الأثير O) وصفتان يمثلان التركيب الجزيئي (الوزن الجزيئي) ومقدار التفرعات (مثل التفرع CH_3 للمثيل) تم استخدامها للتنبؤ بخصائص الوقود.

لتطوير نماذج SP و TSI و OESi باستخدام التعلم الآلي أو أحد أدوات مبدأ الذكاء الاصطناعي (ANN)، تم استخدام البيانات التجريبية لنقاط دخان الوقود والميزات العشر المذكورة أعلاه كمخرج واحد وعشرة مدخلات على التوالي . أظهرت النتائج أن الارتباطات بين SP و TSI و OESi المقاسة والمتوقعة كانت 98% و 97% و 99.9% على التوالي. أيضاً ، كان متوسط الأخطاء المطلقة للقيم المتوقعة 4.5 و 2.5.

أخيراً ، تم توصيف بعض خلطات الوقود والمواد الوقودية التي تحتوي على الأكسجين باستخدام تقنيات تحليلية مختلفة مثل :تقنية تحليل الكربون والهيدروجين والنيتروجين والكبريت (CHNS) ، والتقنيات الطيفية (الأشعة السينية المشتتة للطاقة (EDX) ، والمسح الإلكتروني بالمجهر (SEM) ، المجهر الإلكتروني عالي الدقة (HR-TEM) ، مطياف RAMAN ، التحليل الحراري الوزني (TGA) ، والرنين المغناطيسي النووي ((NMR) ، وانحراف الأشعة السينية ((XRD))

Chapter 1: Introduction

1.1 Thesis Motivation

Soot is usually produced as a byproduct [1] from the incomplete combustion of chemicals (e.g., fuel and oil), materials (e.g., wood and polymers), and domestic waste (e.g., food scraps and plastics) containing carbon. This soot, or black carbon, typically consists of small particles. Here, we are interested in the soot produced from carbon-based fuels such as those derived from fossil fuels and biomass [2]. The sooting tendency of fuels results in significant effects not only on human health but also on the environment. The effects of the sooting propensity on the environment, climate change and human health are discussed below[3, 4].

Environmental Impact:

The incomplete combustion of fuel significantly contributes to air pollution, causing a reduction in visibility and forming smog [5]. This results in significant changes in the air components. Consequently, the photosynthesis process is affected due to soot deposition on plants, leading to growth limitations and productivity reductions [6]. Additionally, soot settling on the ground could contaminate water resources and soil, negatively affecting the aquatic ecosystem and productivity. Therefore, these negatives result in destroying biodiversity and the food chain, ultimately causing ecological imbalance[6].

Climate Change:

Increasing the soot particles in the environment leads to an increase in the absorption of sunlight, resulting in raising the temperature of the earth. This causes global warming and ultimately changes the climate. Also, this will negatively reflect on sea levels, weather patterns, and ecosystems, resulting in significant changes. Furthermore, the soot particles absorbing the sunlight cover the snow and ice surfaces, resulting in reducing the reflectivity of the sunlight. This accelerates the disappearance of ice caps, snow packs, and glaciers, leading to water scarcity and an increase in sea levels [2].

Health Impacts:

Dangerous diseases can be caused by subjecting human beings to soot particles. For example, severe effects on human respiratory health could be caused by inhaling soot particles. The small particles penetrate deeply into the lungs and enter the bloodstream resulting in respiratory illnesses such as chronic obstructive pulmonary disease (COPD), lung cancer, and bronchitis. Furthermore, the circulatory system can be negatively affected by the soot particles, resulting in the risk of strokes, heart attacks, and other circulatory diseases. In addition, the cancer can be primarily caused by specific hydrocarbons like polycyclic aromatic hydrocarbons (PAHs)[7]. For example, developing lung cancer could be increased by continuing exposure to high levels of soot particles.

Given these adverse effects, addressing the propensity of fuels to produce soot is crucial. Various methods have been studied, including cleaner combustion [9] technologies [8], transitioning to cleaner fuel sources[10-14], and blending fossil fuels with zero particulate matter (PM) emissions fuels. In this work, our focus is on studying the latter method, as it is simpler, more implementable, and has been previously applied and proven realistic.

However, experimental measurement of fuel properties, such as sooting tendency, requires expensive instrumentation and experienced technicians and is time-consuming. Hence, there is a need to develop new approaches, including mathematical models, to predict fuel properties, thereby reducing time and cost. Mathematical models can be based on approaches such as the functional group approach [15] and machine learning techniques like ANN [16], which establish the relationship between fuel composition and properties.

We hypothesized that the knowledge of consistent functional groups can be used to predict fuel properties, as fuels consist of a vast number of hydrocarbons made up of a small number of functional groups. Therefore, identifying and quantifying these functional groups can provide a simple method to summarize the different molecular information of fuels and predict their properties. This thesis aimed to achieve several objectives. Firstly, it involved measuring the sooting propensity (SP) of hydrocarbon-oxygenates blends. Secondly, it focused on characterizing various types of fuels (e.g., diesel, diesel-oxygenates blends, and gasoline) using Nuclear Magnetic Resonance (^1H NMR) for functional group determination. Thirdly, the thesis utilized the measured data and functional groups as output and input, respectively, for predicting the sooting tendencies (e.g., SP, TSI, and OESi) of fuels using machine learning-based tools like artificial neural networks (ANN). Furthermore, the developed ANN models were validated using experimental data. Lastly, the hydrocarbons-oxygenates blends were characterized by a CHNS analyzer and spectroscopic techniques such as EDX, SEM, TEM, Raman spectrometry, TGA, and NMR, as well as X-ray diffraction (XRD).

1.2 Thesis Objectives

- i.To measure the smoke point of hydrocarbons-oxygenates blends.
- ii.To Develop predictive models using ANN to predict the following properties of sooting tendency of oxygenated fuels:
 - SP
 - TSI
 - OESi
- iii.To Validate the developed ANN models using experimental data
- iv.To Characterize the soot obtained from combustion of oxygenated fuel in a SP lamp using these techniques: a CHNS analyzer; spectroscopic techniques like EDX, SEM, TEM, Raman spectrometry, TGA and NMR; and X-ray diffraction (XRD).

1.3 Methodology

In accordance with ASTM-D1322, the SP of oxygenate-hydrocarbon blends was measured using a SP lamp apparatus. ANN models were developed based on the measured SP, TSI, or OESi. Additionally, soot formed by the oxygenate-hydrocarbon mixture was collected and characterized using various spectroscopic methods, including EDX, SEM, TEM, Raman spectrometry, TGA, NMR, X-ray diffraction (XRD), and CHNS analysis.

The proposed methodology for developing the ANN began with creating the training set, comprising data from experimental results and published literature. This set was divided into K number of "folds" or subsamples. One-fold served as the validation set, while the remaining folds were used for training the model. "This was rotated until each fold has

been tested on. The evaluation of the model consists of the average over the K tested folds. Based on this evaluation, the following hyperparameters were tuned: the number of units per layer, regularization (common method for combating over-fitting) coefficients, and the number of layers. Each node in the network has an associated weight that is directly proportional to the influence of that feature. For this study, feed-forward neural networks were used, wherein the data moves in a single direction: from the input layer to the output. After a certain number of iterations, also known as epochs, the above process was led to a local minimum for each specific ANN and dataset. Multiple feed-forward architectures (topology of the model) were tested to arrive at the models that give the best results. Finally, the ANN was retrained on all the folds (the original training set) and evaluated on the test set, which led to a robust model.

Chapter 2: Smoke point prediction of oxygenated fuels using neural networks.

Under both steady and transient states, compression-based ignition (CI) engines exhibit higher efficiency in energy conversion than spark-based ignition (SI) engines. However, CI engines emit relatively high concentrations of particulate matter (PM) and nitrogen oxides (NO_x) [38]. SI engines with direct-injection system show considerably high PM emissions compared to manifold injected engines thereby requiring the implementation of filters in the gas exhaust [39]. In this regard, the emissions of NO_x and PM from new vehicles must meet the current Environmental Protection Agency (EPA) 2010 and Euro 6 emission standards, respectively [40, 41].

To reduce the emissions of the abovementioned pollutants, which mostly comprise PM emitted from vehicles, one approach involves using clean oxygenated fuels. The PM emission from engines is affected by the type of fuel and engine condition. Generally, the SP is one of the optimal indices for evaluating the sooting tendencies of various fuels [33, 42-44]. The SP of fuel is used to calculate the TSI [45] which is a widely used index for numerically quantifying the sooting tendency of a fuel. The SP is an important index for assessing the quality of jet fuels and kerosene. It is used to measure the tendency of fuels to form smoke when burning. The smoke formation is attributed to the incomplete combustion of carbonaceous particles, which is detrimental to humans, engines, and the environment. Conventionally, the SP of fuel is determined using a specific test burner equipped with a scale. The fuel is burned, and the flame height where smoke formation

begins is marked as the SP. Thus, fuels that exhibit high SPs are desired. In this regard, hydrocarbons such as naphthenes and aromatics which produce low SPs are considered the primary drivers of soot formation [46].

The SP of fuel—such as kerosene, jet fuel, and diesel—refers to the maximum height (in mm) of the flame formed via diffusion under standard conditions, after which smoke formation begins. Overall, fuels with high aromatic contents produce considerable smoke. When the content of aromatics is high, the flame height is low. Therefore, fuels exhibiting a high SP show a low sooting tendency [47]. Among hydrocarbons, paraffins exhibit the highest SP followed by naphthenes and aromatics. Because paraffins show high SPs, they exhibit a low sooting tendency (produce less smoke); the opposite is true for aromatic compounds. For example, the average SPs of kerosene and diesel produced from a refinery [48] are 24.6 and 19 mm, respectively [49]. The relatively low SP of diesel indicates that it has a higher sooting tendency than kerosene because it contains high contents of aromatics. This comparison proves the direct relation between the sooting tendency and aromaticity (carbon atoms included in petroleum fractions). Therefore, top and bottom products from distillation towers show the lowest and highest sooting tendencies, respectively. In refineries, because aromatic-containing fuels contribute to the formation of carbon when they are burned, some aromatics are extracted, which increases the SP of the fuels to ~20 mm [50].

Generally, the SP is measured for various purposes, including selecting specific oils for heating, cooking, burning, or lighting depending on the apparatus; classifying fuel quality; and maintaining high environmental cleanliness and safety. In addition, the measurement of the SP can significantly enable the design of a high-efficiency nonsmoker-generating

apparatus. For example, lighting lamps produce soot (smoke) when the wick height is increased. Regarding quality, the fuel quality can be determined by measuring the SP. For example, kerosene samples obtained from various refineries can be compared using properties such as the SP, specific gravity, cloud point, freezing point, and flash point. Thus, the SP measurement is important for determining the quality of kerosene. From environmental and safety perspectives, the SP data of fuels can be beneficial for preventing health issues and decreasing environmental damage. For example, when kerosene is burned in a closed room and smoke is produced, toxic gases that deteriorate human health and pollute the air are produced. To improve the SP of fuels such as kerosene, the sooting tendency must be reduced. This can be achieved by increasing the content of paraffinic groups and decreasing the C/H ratio by increasing the number of hydrogen atoms. Experimental measurement of the SP is carried out based on the ASTM D1322-19 standard and the following steps are involved: (1) the SP lamp apparatus used is calibrated and adjusted, (2) experiments are performed on an uninclined surface, (3) a specific wick is used, (4) air currents should be avoided in the experimental environment, and (5) the observer should carefully position oneself to read the SP from the lamp scale.

Blending petroleum fuels with biomass-derived oxygenated additives [51-54] (which are renewable sources) is a successful strategy for reducing soot formation in the exhaust of engines. Because biomass-derived fuels (e.g., alcohols and ethers) show a low sooting tendency [30, 51-53, 55-57], they have been utilized to reduce soot emissions. Furthermore, these two types of fuels are frequently mixed to enhance the features of the parent fuel [58]. Note that the SP of the compounds/mixtures must be determined to determine their sooting tendencies. However, conducting experiments in the lab for numerous fuel samples is

difficult and time-consuming. Therefore, a mathematical model is required to predict and screen the SP of fuels for bulk analyses.

This study aims to develop a model for the prediction of SP of petroleum fuels and surrogate blends, including those containing alcohol and ethers as additives. Thus, expressing the molecular structure of fuels in terms of functional groups (e.g., CH₃ and CH₂) [15, 16, 58-60] can sufficiently improve the predictive model of the SP. Furthermore, the functional groups have been exploited to determine certain properties, such as the sooting tendency [61], flash point [24], autoignition point [62], and ignition delay [63]. Research has shown that the functional groups in fuels influence their combustion, chemical, and physical behaviors [64]. Based on their functional groups, fuels can be divided into paraffinic CH₃, CH₂, CH, olefinic CH–CH₂, naphthenic–CH=CH₂, aromatic C–CH, alcohol OH, and ether O groups. These eight groups can serve as inputs for improving the SP-prediction model. Furthermore, because the molecular weight (MW) and branching index (BI) of fuels affect their physical properties, such as their density and vaporization point, they are included along with the functional groups as inputs, affording 10 inputs to the model.

Linear methods such as multiple linear regression (MLR) cannot accurately capture the relation between the 10 inputs and the output of the SP-prediction model. The performance of MLR was investigated using the developed datasets, achieving a low correlation coefficient (R^2) of 0.84. Therefore, an accurate SP-prediction model is required for capturing nonlinear trends, particularly when mixing more than two compounds [65]. Generally, linear regression models—such as partial least squares (PLS) and MLR—cannot capture all the relations between the inputs and output of the model. To overcome

this issue, an artificial intelligence (AI)–based method—such as machine learning—can be used. A common tool of machine learning is an ANN, which is suitable for addressing this problem. The study aims to apply ANNs to predict the SP of fuels with known fuel compositions (eight functional groups, MW, and BI). Figure 1 presents the general architecture of an ANN. The inputs are represented in the first column (input layer), and the hidden layers, from the first hidden layer (hidden layer 1) to the last hidden layer (hidden layer n), are represented in the middle columns. The outputs are represented in the last column (target layer). Every layer contains several neurons, represented as nodes. In the figure, the number of inputs corresponds to the number of nodes in the first layer, and the output is represented as one node in the last layer. The neurons are represented as nodes in the hidden layers.

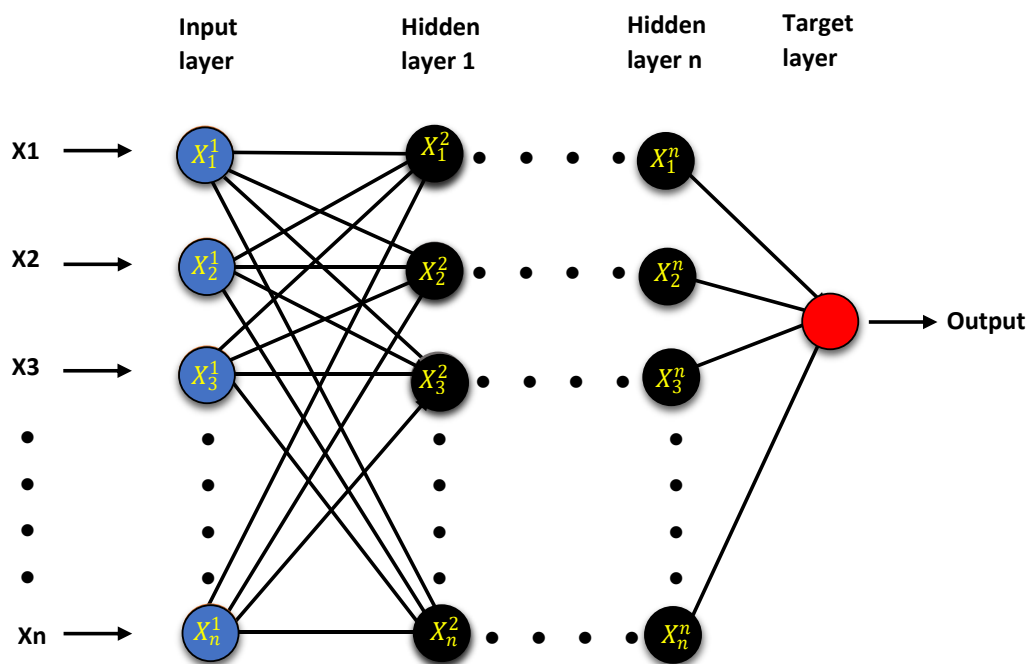


Fig. 1. Schematic of an ANN.

2.1 Experimental Section

2.1.1 Materials

A standard SP lamp from Koehler, USA was used for performing the measurements. n-Heptane, toluene, and *iso*-octane (2,2,4-trimethylpentane) were purchased from Sigma Aldrich each having a minimum purity of 99.5%. Ethers (diethyl ether, dibutyl ether, dioctyl ether, tert-butyl-methyl ether (TBME), and diphenyl ether) were purchased from Sigma Aldrich with a minimum purity of 99% for each of the chemicals. Gasoline and diesel samples were obtained from a filling station in Dhahran, Saudi Arabia.

2.1.2. Experimental procedure for SP measurement

The experiments were conducted according to the ASTM D1322 standard. Briefly, all the tools—including a sharp razor or wick trimmer, candle, and wick tube—were cleaned three times using deionized water and n-heptane at the beginning of each experiment. Next, a dried cotton wick was soaked in the prepared fuel sample and then correctly inserted in the wick tube without frayed ends and twists using a wick inserter and trimmer. Next, the wick tube was placed in a dried candle which possessed around 20-25 mL of the fuel; the air vent was sample-free. Next, the candle was carefully inserted into the SP lamp. Next, the wick was adjusted to a 10 mm flame height. After continuously burning for a period of 5 min, the candle was lifted until a tail of smoke appeared. Thereafter, the candle was gradually lowered at short intervals until no smoke was observed. The scale of the SP lamp was used to read the maximum height (± 0.5 mm) of the flame without smoke. This last step was repeated three times to ensure high precision (the difference between the values was not more than 1 mm). Finally, the average of the three readings was used as the measurement data. Figure 4 shows the flame image for a

fuel blend consisting of 20% diphenyl ether and 80% diesel by volume. The reference compounds namely toluene and *iso*-octane were tested using the SP lamp before the experiments to ensure that the difference between the standard references and our results was not more than 1 mm. All the SP values were close to those of the standard references, with a difference of less than 1 mm.



Fig. 2. SP measurement of fuel blend consisting of diphenyl ether (20%) and diesel (80%) by volume.

2.1.3 ^1H NMR spectroscopy

^1H NMR spectroscopy measurements of the gasoline and diesel samples were carried out for identifying and quantifying the functional groups in the samples. The obtained samples were stored in a refrigerator before ^1H -NMR measurements to prevent the escape of volatile components. Two 500- μL portions of deuterated chloroform (CDCl_3) were mixed with two 50- μL samples of gasoline and diesel at ambient temperature. Generally, CDCl_3 is used as a solvent because it does not contain H atoms for producing peaks in the ^1H -NMR spectrum. Small amounts of the CDCl_3 -gasoline and

–diesel mixtures were poured into small tubes for standard NMR analysis. A 400-MHz Bruker spectrometer was employed for the ^1H -NMR measurements at 298 K. For each mixture, 128 scans were performed at 5-s intervals (as the recycle delay). A pulse sequence of 90° and a one-dimensional pulse program was adopted along with the standard program “zg” in the Bruker library; tetramethyl silane (TMS) was used as the internal standard. A spectral width of 14,098 Hz digitized into 64K data points was employed for recording the free-induction decay signals. TopSpin software was used to record the ^1H -NMR spectra. Figure 5 shows the ^1H -NMR spectra of the gasoline and diesel samples.

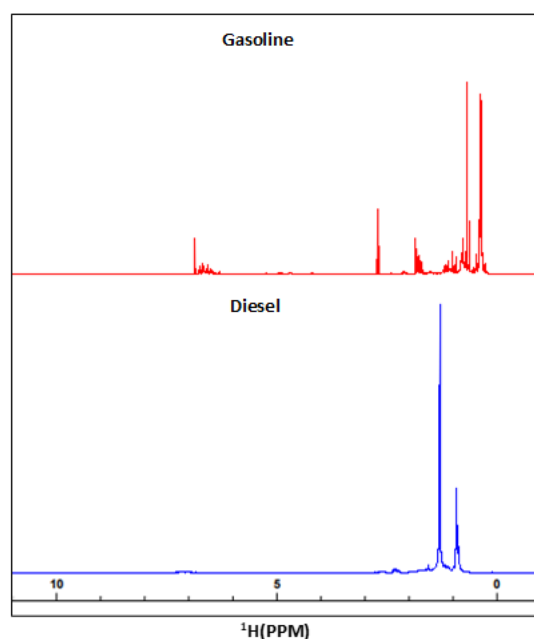


Fig. 3. ^1H -NMR spectra of gasoline and diesel samples.

2.2 METHODOLOGIES

2.2.1 Dataset

A dataset of 366 fuel samples comprising 8 gasoline and diesel, 113 pure compounds (37 paraffins, 19 olefins, 13 naphthenes, 30 aromatics, 6 alcohols, and 8 ethers), and 245 mixtures of fuel blends was employed. The dataset used herein was obtained from the literature [15, 31, 33, 66-78] and the present work. All the data, including the SP values of pure compounds and the mixture compositions, are provided in the following Tables 1 and 2, respectively.

Table 1: SP of pure compounds

S.No.	Name	SP (mm)	Uncertainty	References
	Paraffins			
1.	ethane	319	47.96%	[1]
2.	propane	202	40.59%	[1]
3.	n-butane	175	18.86%	[1]
4.	isobutane	96.3		[1]
5.	n-pentane	163	15.34%	[1]
6.	isopentane	104		[1]
7.	2,2-dimethylpropane	59.8		[1]
8.	n-hexane	149	16.11%	[1]
9.	2-methylpentane	116	6.03%	[1]
10.	3-methylpentane	124	9.68%	[1]

11.	2,2-dimethylbutane	80.1	47.44%	[1]
12.	2,3-dimethylbutane	105		[1]
13.	n-heptane	139	10.79%	[1]
14.	2-methylhexane	119		[1]
15.	3-methylhexane	120		[1]
16.	2,3-dimethylpentane	107		[1]
17.	2,4-dimethylpentane	102		[1]
18.	n-octane	137	20.44%	[1]
19.	2-methylheptane	120		[1]
20.	3-methylheptane	110		[1]
21.	4-methylheptane	102		[1]
22.	3-ethylhexane	102		[1]
23.	2,2-dimethylhexane	87.3		[1]
24.	2,3-dimethylhexane	107		[1]
25.	2,2,4-trimethylpentane	54.3	23.94%	[1]
26.	2,3,4-trimethylpentane	59		[1]
27.	2-methyle-3-ethylpentane	89		[1]
28.	n-nonane	110	24.55%	[1]
29.	isononane	129		[1]

30.	n-decane	122	11.48%	[1]
31.	n-undecane	113	20.35%	[1]
32.	n-dodecane	107	22.43%	[1]
33.	n-tridecane	116		[1]
34.	n-tetradecane	120		[1]
35.	iso-cetane	31.2		[2]
36.	hexadecane	110		[1]
37.	iso-dodecane	35.2		[2]
	OLEFINS			
38.	ethylene	120	15.00%	[1]
39.	propylene	32.8	14.33%	[1]
40.	1,3-butadiene	9.23	119.18%	[1]
41.	1-butene	29.1		[1]
42.	2-butene	30.7		[1]
43.	isobutene	22.6	32.74%	[1]
44.	1-pentene	47.1	19.53%	[1]
45.	1-hexene	55.2	22.64%	[1]
46.	1-heptene	70.1	22.25%	[1]
47.	cis 2-heptene	73.8	14.91%	[1]

48.	1-octene	56.7	36.86%	[1]
49.	trans 2-octene	86.4		[1]
50.	1-nonene	55.2		[1]
51.	1-decene	72.4	24.86%	[1]
52.	1-dodecene	68.3	44.36%	[1]
53.	1-tridecene	55.2		[1]
54.	1-tetradecene	67.9	33.28%	[1]
55.	1-hexadecene	69.2	36.27%	[1]
56.	1 octadecene	82.1		[1]
	NAPHTHENES			
57.	cyclopropane	25.9		[1]
58.	cyclopentane	58	23.28%	[1]
59.	cyclopentene	10.3		[1]
60.	methyl cyclopentane	55.3	1.99%	[1]
61.	cyclohexane	81.9	20.02%	[1]
62.	cyclohexene	38.7	16.28%	[1]
63.	methylcyclohexane	56.6	14.20%	[1]
64.	1,3-dimethylcyclohexane	61.1		[1]
65.	ethyl cyclohexane	71.3	34.50%	[1]

66.	cyclooctane	56.4		[1]
67.	decalin	25.5	16.86%	[1]
68.	4-methylcyclohexene	23.5		[1]
69.	bicyclohexyl	42.9		[1]
	AROMATICS			
70.	benzene	8.79	18.89%	[1]
71.	toluene	8.12	19.70%	[1]
72.	styrene	5.27	66.22%	[1]
73.	ethylbenzene	5.92	16.89%	[1]
74.	indene	5.99	3.84%	[1]
75.	1,3-dimethylbenzene	7		[3]
76.	1,4-dimethylbenzene	7		[3]
77.	1,2-dimethylbenzene	8.1	20.00%	[1]
78.	1,2,3-trimethylbenzene	6.43	18.20%	[1]
79.	1,3,5-trimethylbenzene	5.24		[1]
80.	1,2,4-trimethylbenzene	6		[3]
81.	propyl benzene	6.86	27.70%	[1]
82.	isopropyl benzene	6.14	28.99%	[1]
83.	naphthalene	3.49		[1]

84.	1,2-dihydronaphthalene	5.57		[1]
85.	tetralin	7.4	16.35%	[1]
86.	1,2-diethylbenzene	6.11		[1]
87.	4-Isopropyltoluene	7.9	35.95%	[1]
88.	n-butylbenzene	7.39	28.69%	[1]
89.	1-methylnaphthalene	5.14	9.34%	[1]
90.	tert-pentyl benzene	6.98		[1]
91.	sec-pentyl benzene	6.98		[1]
92.	n-pentyl benzene	10.6		[1]
93.	1,2-dimethylnaphthalene	4.37		[1]
94.	cyclohexylbenzene	7.67	13.82%	[1]
95.	1,3-diisopropylbenzene	10.6		[1]
96.	s-butylbenzene	6.97	24.25%	[1]
97.	tert-butylbenzene	4.37		[1]
98.	2-methylnaphthalene	4.37		[1]
99.	1,2-dimethylnaphthalene	4.37		[1]
	ALCOHOLS			
100.	1-butanol	31.3		[4]
101.	1-pentanol	27.7		[4]

102.	2-pentanol	29.1		[4]
103.	3-methyl 1-butanol	26.3		[4]
104.	2-methyl 1-butanol(2-Methylbutan-1-ol)	24.8		[4]
105.	2-methyl 2-butanol	25.9		[4]
	ETHERS			
106.	dimethoxymethane	25.4		[4]
107.	methyl sec-butyl ether	28.5		[4]
108.	methyl tert-butyl ether	24.1		[4]
109.	1,2-dimethoxyethane	24.4		[4]
110.	diethylene glycol methyl ether	39.4		[4]
111.	ethylene glycol monopropyl ether	26.7		[4]
112.	2,2-dimethoxypropane	25.9		[4]
113.	diphenyl ether	5	10%	This work
	real fuels			
114.	Face A gasoline)	67.9	27.54%	[5]
115.	Face C gasoline)	49.8	9.64%	[5]
116.	Face F gasoline)	37.4	2.67%	[5]
117.	Face G gasoline)	15.6	6.41%	[5]
118.	Face I gasoline)	102.1	55.73%	[5]
119.	Face J gasoline)	18	5.56%	[5]

120.	Saudi gasoline	15	3.33%	This work
121.	Saudi diesel	29.5	1.69%	This work

Table 2: SP of mixtures

S.No	Mixtures	SP	Uncertainty	Ref.
1.	3-methylpentane /Tetralin (94/6 mol%)	44.8	7.37%	[5]
2.	3-methylpentane/Indane (80/20 mol%)	18.4	5.43%	[5]
3.	3-methylpentane /Tetralin (70/30 mol%)	14.4	6.94%	[5]
4.	3-methylpentane/Tetralin (68/32 mol%)	15	6.67%	[5]
5.	n-heptane/Toluene (53/47 mol%))	18.8	5.32%	[5]
6.	iso-octane/toluene (60/40 Vol%)	14.56842	3.50%	[6]
7.	iso-octane/ toluene (75/25 Vol%)	19.9	2.56%	[6]
8.	iso-octane/ toluene (80/20 Vol%)	21.7	2.35%	[6]
9.	iso-octane/ toluene (85/15 Vol%)	24.6	2.07%	[6]
10.	iso-octane/ toluene (90/10 Vol%)	29.43333	1.73%	[6]
11.	iso-octane/ toluene (95/5 Vol%)	31.6	1.61%	[6]
12.	iso-cetane/ 1,2,4 TMB (11/89 Vol%)	8.1	6.30%	[6]
13.	iso-cetane/ 1,2,4 TMB (24/76 Vol%)	10.2	5.00%	[6]
14.	iso-cetane/ 1,2,4 TMB (42/58 Vol%)	11.9	4.29%	[6]
15.	iso-cetane/ 1,2,4 TMB (53/47Vol%)	14.2	3.59%	[6]

16.	iso-cetane/ 1,2,4 TMB (66/34Vol%)	18.5	2.76%	[6]
17.	iso-cetane/ 1,2,4 TMB (81/19 Vol%)	24.5	2.08%	[6]
18.	iso-octane / toluene (10/90 Vol%)	8.4	6.07%	[6]
19.	iso-octane /toluene (24/76 Vol%)	10.2	5.00%	[6]
20.	iso-octane / toluene (39/61 Vol%)	12.3	4.15%	[6]
21.	iso-octane /toluene (49/51 Vol%)	14.5	3.52%	[6]
22.	iso-octane /toluene (66/34 Vol%)	20	2.55%	[6]
23.	iso-octane /toluene (72/28 Vol%)	21.7	2.35%	[6]
24.	iso-octane /toluene (78/22 Vol%)	24.6	2.07%	[6]
25.	iso-octane / toluene (85/15 Vol%)	29.4	1.73%	[6]
26.	iso-octane /toluene (92/8 Vol%)	35	1.46%	[6]
27.	m-xylene / n-dodecane (17/83 Vol%)	36.9	1.38%	[6]
28.	m-xylene / n-dodecane (33/67 Vol%)	26.8	1.90%	[6]
29.	m-xylene / n-dodecane (34/66 Vol%)	26.4	1.93%	[6]
30.	m-xylene / n-dodecane (36/64 Vol%)	23.9	2.13%	[6]
31.	m-xylene /n-dodecane (37/63Vol%)	24	2.13%	[6]
32.	m-xylene / n-dodecane (39/61 Vol%)	23	2.22%	[6]
33.	m-xylene /n-dodecane (50/50 Vol%)	19.5	2.62%	[6]
34.	m-xylene / n-dodecane (65/35 Vol%)	14.1	3.62%	[6]

35.	m-xylene / n-dodecane (78/22 Vol%)	11.9	4.29%	[6]
36.	m-xylene / n-dodecane (88/12 Vol%)	9.8	5.20%	[6]
37.	75%1,2,4 TMB / 1-MN (75/25 Vol%)	6.9	7.39%	[6]
38.	1,2,4 TMB / 1-MN (60/40 Vol%)	6.2	8.23%	[6]
39.	1,2,4 TMB / 1-MN (40/60 Vol%)	6.2	8.23%	[6]
40.	1,2,4 TMB / 1-MN (25/75 Vol%)	6.2	8.23%	[6]
41.	decalin / 1-MN (95/5 Vol%)	20	2.55%	[6]
42.	decalin / 1-MN (89/11 Vol%)	17.4	2.93%	[6]
43.	decalin / 1-MN (78/22 Vol%)	13.3	3.83%	[6]
44.	decalin / 1-MN (68/32 Vol%)	11.3	4.51%	[6]
45.	decalin / 1-MN (52/48 Vol%)	9.2	5.54%	[6]
46.	decalin / 1-MN (32/68 Vol%)	7.2	7.08%	[6]
47.	decalin / 1-MN (13/87 Vol%)	6.1	8.36%	[6]
48.	MCH / 1-MN (98/2 Vol%)	29.9	1.71%	[6]
49.	MCH / 1-MN (95/5 Vol%)	23.7	2.15%	[6]
50.	MCH / 1-MN (91/9 Vol%)	18.9	2.70%	[6]
51.	MCH / 1-MN (81/19 Vol%)	14.7	3.47%	[6]
52.	MCH / 1-MN (72/28 Vol%)	11.5	4.43%	[6]
53.	MCH / 38%1-MN (62/38 Vol%)	10.5	4.86%	[6]

54.	MCH /1-MN (42/58 Vol%)	7.3	6.99%	[6]
55.	MCH /1-MN (21/79 Vol%)	6.3	8.10%	[6]
56.	toluene / isooctane / n-heptane (66.7/16.67/16.67 Vol%)	10.8	12.04%	[7]
57.	toluene / isooctane (50/50 Vol%)	8.9	10.11%	[7]
58.	toluene/ isooctane / n-heptane (33.3/33.3/33.3 Vol%)	16.5	18.79%	[7]
59.	toluene / isooctane / n-heptane (16.67/66.7/16.67 Vol%)	21.7	11.98%	[7]
60.	toluene/ isooctane/ n-heptane (16.67/16.67/66.7 Vol%)	25.7	28.79%	[7]
61.	isooctane / n-heptane (50/50 Vol%)	53.2	13.16%	[7]
62.	n-heptane/ toluene (50/50 mol%)	11.1	7.40%	[7]
63.	n-heptane/ toluene (66/33 mol%)	14.9	8.40%	[7]
64.	n-heptane/ toluene (75/25 mol%)	17.5	11.10%	[7]
65.	isooctane/ toluene (50/50 mol%)	8.9	10.11%	[7]
66.	isooctane/ toluene (60/40 mol%)	11.2	10.71%	[7]
67.	Isooctane/ toluene (66/33 mol%)	11.9	19.33%	[7]
68.	isooctane/toluene (75/25 mol%)	16.7	9.58%	[7]
69.	isooctane/ toluene (80/20 mol%)	18.1	12.15%	[7]
70.	isooctane/ toluene (90/10 mol%)	24	14.58%	[7]

71.	isooctane/ toluene (95/5 mol%)	30.7	14.01%	[7]
72.	n-heptane / toluene (90/10 Vol%)	39	7.18%	[8]
73.	n-heptane /toluene (70/30 Vol%)	20.5	8.29%	[8]
74.	n-heptane /toluene (50/50 Vol%)	12	9.17%	[8]
75.	n-heptane /toluene (30/70 Vol%)	9.8	8.16%	[8]
76.	naphthalene /heptane/ toluene (15/55.25/29.75 Vol %)	9.9	3.64%	[9]
77.	naphthalene / heptane/toluene (10/58.5/31.5 Vol %)	12	5.17%	[9]
78.	naphthalene/ heptane/ toluene (5/61.75/33.25 Vol %)	14.33	4.95%	[9]
79.	tetralin / heptane/ toluene (40/36/24 Vol %)	9.1	2.20%	[9]
80.	tetralin/ heptane/ toluene) (20/52/280 Vol %)	12.4	3.71%	[9]
81.	tetralin / heptane/toluene (10/58.5/31.5 Vol %)	14.43	4.30%	[9]
82.	cyclopentene / heptane/ toluene (60/26/14 Vol%)	13	1.46%	[9]
83.	cyclopentene / heptane/toluene (40/26/14 Vol%)	14.2	1.55%	[9]

84.	cyclopentene / heptane/ toluene (20/26/14 Vol%)	15.5	3.23%	[9]
85.	n-octane /heptane/ toluene (10/58.5/31.5 Vol%)	20.03	1.40%	[9]
86.	n-octane/ heptane/ toluene (20/52/28 Vol%)	21.13	1.47%	[9]
87.	n-octane/ heptane/ toluene (40/39/21 Vol%)	25.77	0.85%	[9]
88.	n-octane / heptane/ toluene (60/26/14 Vol%)	32.65	1.23%	[9]
89.	1-methylnaphthalene / heptane/ toluene (15/55.25/29.75 Vol%)	9.9	4.04%	[9]
90.	1-methylnaphthalene / heptane/ toluene (10/58.5/31.5 Vol%)	11.61	1.98%	[9]
91.	1-methylnaphthalene /heptane/ toluene (5/61.75/33.25 Vol%)	13.57	1.84%	[9]
92.	benzene / heptane/ toluene (40/58.5/31.5Vol%)	9.79	2.04%	[9]
93.	benzene / heptane/ toluene (20/58.5/31.5Vol%)	11.92	3.44%	[9]
94.	benzene / heptane/ toluene) (10/58.5/31.5 Vol%)	14.42	2.29%	[9]
95.	n-heptane /Toluene (60/40 Vol%)	15.05	5.05%	[9]

96.	n-heptane / Toluene (65/55 Vol%)	16.92	2.84%	[9]
97.	n-heptane / Toluene (80/20 Vol%)	27.94	1.43%	[9]
98.	n-heptane / Toluene (90/10 Vol%)	37.79	1.14%	[9]
99.	toluene/ iso-octane (20/80 Vol%)	22.8	1.27%	[9]
100.	toluene/ iso-octane (10/90 Vol%)	31.2	10.96%	[9]
101.	toluene/ iso-octane (5/95 Vol%)	34.2	9.65%	[9]
102.	iC8/iC16 (50/50 mol%)	34.1		[2]
103.	n-dodecane / iso-cetane/ decalin/ Toluene (47.06/16.69 /24.19/12.06 Vol%)	28.5		[10]
104.	n-dodecane/ iso-cetane / isooctane/ decalin) (14.16 /31.41 /40.16 /14.27 Vol%)	37.1		[10]
105.	n-dodecane/ iso-octane/1,3,5- trimethylbenzene/ n-propyl benzene (40.41 /29.48 /7.28 /22.83 mol%)	22.5		[11]
106.	n-hexadecane/1,2,4 trimethylbenzene (85/15 Vol%)	32	1.59%	[12]
107.	n-hexadecane/ 1,2,4 trimethylbenzene (80/20 Vol%)	26	1.96%	[12]
108.	n-hexadecane/ 1,2,4 trimethylbenzene (75/15 Vol%)	20	2.55%	[12]
109.	n-hexadecane/ 1,2,4 trimethylbenzene (70/30 Vol%)	16.8	3.04%	[12]

110.	n-hexadecane/1,2,4 trimethylbenzene (65/35 Vol%)	15	3.40%	[12]
111.	n-hexadecane/1,2,4 trimethylbenzene (6/4 Vol%)	13.8	3.70%	[12]
112.	n-hexadecane/1,2,4 trimethylbenzene (5/5 Vol%)	11.5	4.43%	[12]
113.	tri (propylene glycol) methyl ether/ 1,2,4 trimethylbenzene (8/20 Vol%)	32	1.59%	[12]
114.	tri (propylene glycol) methyl ether /1,2,4 trimethylbenzene (75/25 Vol%)	22	2.32%	[12]
115.	tri (propylene glycol) methyl ether/1,2,4 trimethylbenzene (70/30 Vol%)	17.7	2.88%	[12]
116.	tri (propylene glycol) methyl ether/ 1,2,4 trimethylbenzene) (65/35 Vol%)	15	3.40%	[12]
117.	tri (propylene glycol) methyl ether/1,2,4 trimethylbenzene (6/4% Vol%)	12.5	4.08%	[12]
118.	tri (propylene glycol) methyl ether/ 1,2,4 trimethylbenzene (50/50 Vol%)	10	5.10%	[12]
119.	tri (propylene glycol) methyl ether/1,2,4 trimethylbenzene (20/80 Vol%)	7.5	6.80%	[12]
120.	tri (propylene glycol) methyl ether/ 1,2,4 trimethylbenzene (70/30 Vol%)	17.8	2.87%	[12]

121.	tri (propylene glycol) methyl ether/n-hexadecane/1,2,4 trimethylbenzene) (50/20/30 Vol%)	18	2.83%	[12]
122.	tri (propylene glycol) methyl ether/n-hexadecane/1,2,4 trimethylbenzene (23/47/30 Vol%)	18	2.83%	[12]
123.	tri (propylene glycol) methyl ether/n-hexadecane/1,2,4 trimethylbenzene (11/59/30 Vol%)	18	2.83%	[12]
124.	tri (propylene glycol) methyl ether/ 1,2,4 trimethylbenzene (50/50 Vol%)	10.7	4.77%	[12]
125.	tri (propylene glycol) methyl ether/n-hexadecane/1,2,4 trimethylbenzene (23.5/26.5/50 Vol%)	11	4.64%	[12]
126.	TPGME (tri (propylene glycol) methyl ether/ n-hexadecane/1,2,4 trimethylbenzene (11.5/38.5/50 Vol%)	11.2	4.55%	[12]
127.	n-hexadecane/ 1,2,4 trimethylbenzene (50/50 Vol%)	11.2	4.55%	[12]
128.	1-butanol/ 1,2,4 trimethylbenzene (70/30 Vol%)	20	2.55%	[12]
129.	1-butanol/n-hexadecane/1,2,4 trimethylbenzene (38/32/30 Vol%)	19.5	2.62%	[12]

130.	1-butanol/ n-hexadecane/1,2,4 trimethylbenzene (18.5/51.5/30 Vol%)	19.2	2.66%	[12]
131.	2,2,4,4,6,8,8-heptamethylnonane/ 1,2,4 trimethylbenzene (70/30 Vol%)	16.8	3.04%	[12]
132.	2,2,4,4,6,8,8-heptamethylnonane/n-hexadecane/1,2,4 trimethylbenzene (35/35/30 Vol%)	14.8	3.45%	[12]
133.	1-undecanol/ 1,2,4 trimethylbenzene (70/30 Vol%)	19.8	2.58%	[12]
134.	1-undecanol /n-hexadecane/1,2,4 trimethylbenzene (43.5/26.5/30 Vol%)	19	2.68%	[12]
135.	isooctane/ decalin/1,3,5-trimethylbenzene (35/35/30 Vol%)	15.89	3.59%	[13]
136.	n-tetradecane/ decalin/ 1,3,5-trimethylbenzene (80/5/15 Vol%)	32.56	1.90%	[13]
137.	n-dodecane/ isooctane/ 1,3,5-trimethylbenzene (80/10/10 Vol%)	39.11	1.66%	[13]
138.	n-tetradecane/ isooctane/1,3,5-trimethylbenzene (80/5/15 Vol%)	34.06	1.73%	[13]
139.	decalin/ 1,3,5-trimethylbenzene (90/10 Vol%)	18.17	3.19%	[13]
140.	n-dodecane/ 1,3,5-trimethylbenzene (70/30 Vol%)	18.50	3.30%	[13]

141.	n-dodecane/ n-tetradecane/ isooctane/1,3,5-trimethylbenzene (40/40/10/10 Vol%)	41.72	1.46%	[13]
142.	n-dodecane/n-tetradecane/ isooctane/decalin/1,3,5-trimethylbenzene (47.9/12.9/7.5/7.5/24.2 Vol%)	21.67	2.82%	[13]
143.	n-dodecane/n-tetradecane/ isooctane/decalin/ 1,3,5-trimethylbenzene (52.9/12.9/12.5/7.5/14.2 Vol%)	29.67	2.16%	[13]
144.	n-dodecane/n- tetradecane/isooctane/decalin/ 1,3,5- trimethylbenzene (12.9/52.9/7.5/12.5/14.2 Vol%)	26.83	2.39%	[13]
145.	n-tetradecane/1,3,5-trimethylbenzene (80/20 Vol%)	25.72	2.37%	[13]
146.	n-dodecane/ isooctane/1,3,5- trimethylbenzene (35/35/30 Vol%)	16.28	3.75%	[13]
147.	n-dodecane/n- tetradecane/isooctane/decalin/ 1,3,5- trimethylbenzene (52.9/12.9/7.5/7.5/19.2 Vol%)	24.83	2.46%	[13]
148.	n-dodecane/decalin/1,3,5- trimethylbenzene (35/35/30 Vol%)	16.56	3.74%	[13]
149.	n-dodecane/ isooctane/ 1,3,5- trimethylbenzene (80/5/15 Vol%)	30.61	2.06%	[13]

150.	Isooctane/ 1,3,5-trimethylbenzene (90/10 Vol%)	26.44	2.46%	[13]
151.	n-dodecane /n-tetradecane/ isooctane/decalin/1,3,5-trimethylbenzene (12.9/12.9/7.5/42.5/24.5 Vol%)	16.17	3.77%	[13]
152.	n-dodecane/n- tetradecane/isooctane/decalin/1,3,5- trimethylbenzene (25.8/25.8/15/15/18.3 Vol%)	21.89	2.74%	[13]
153.	n-dodecane/n- tetradecane/isooctane/decalin/1,3,5- trimethylbenzene (12.9/12.9/7.5/52.5/14.2)	20.06	2.94%	[13]
154.	n-tetradecane/1,3,5-trimethylbenzene (75/25 Vol%)	23.89	2.51%	[13]
155.	n-dodecane /decalin/ 1,3,5- trimethylbenzene (80/5/15 Vol%)	31.67	1.93%	[13]
156.	Isooctane/decalin/1,3,5-trimethylbenzene (35/35/30 Vol%)	13.11	4.58%	[13]
157.	Decalin/ 1,3,5-trimethylbenzene (70/30 Vol%)	12.94	4.56%	[13]
158.	n-tetradecane/isooctane/decalin/ 1,3,5- trimethylbenzene (80/5/5/10)	41.17	1.55%	[13]

159.	n-tetradecane/ isooctane/ 1,3,5-trimethylbenzene (80/10/10 Vol%)	39.44	1.65%	[13]
160.	n-dodecane/n-tetradecane/ 1,3,5-trimethylbenzene (40/40/20 Vol%)	27.28	2.35%	[13]
161.	n-tetradecane/ 1,3,5-trimethylbenzene (70/30 Vol%)	19.10	3.40%	[13]
162.	n-tetradecane/ isooctane/1,3,5-trimethylbenzene (40/50/10)	32.61	1.93%	[13]
163.	Isooctane/ 1,3,5-trimethylbenzene (70/30 Vol%)	14.39	4.17%	[13]
164.	decalin/1,3,5-trimethylbenzene (80/20 Vol%)	15.33	3.98%	[13]
165.	n-dodecane/n-tetradecane/ isooctane/decalin/ 1,3,5-trimethylbenzene (12.9/52.9/12.5/7.5/14.2 Vol%)	29.11	2.06%	[13]
166.	n-dodecane/n-tetradecane/ isooctane/decalin/ 1,3,5-trimethylbenzene (12.9/52.9/7.5/7.5/19.2 Vol%)	26.17	2.33%	[13]
167.	n-tetradecane/ isooctane/decalin/1,3,5-trimethylbenzene (35/35/30 Vol%)	16.22	3.76%	[13]
168.	n-dodecane/ isooctane/decalin/ 1,3,5-trimethylbenzene (80/5/5/10 Vol%)	40.61	1.55%	[13]

169.	n-dodecane/n-tetradecane/isooctane/ decalin, 1,3,5-trimethylbenzene (52.9/12.9/7.5/12.5/14.2 Vol%)	27.94	2.22%	[13]
170.	n-dodecane/decalin/ 1,3,5- trimethylbenzene (80/10/10 Vol%)	36.61	1.78%	[13]
171.	n-tetradecane/decalin/1,3,5- trimethylbenzene (40/50/10 Vol%)	24.39	2.46%	[13]
172.	n-tetradecane/ decalin/1,3,5- trimethylbenzene (80/10/10 Vol%)	39.06	1.59%	[13]
173.	Isooctane/decalin/ 1,3,5-trimethylbenzene (45/45/10)	20.78	2.94%	[13]
174.	n-dodecane/n-tetradecane/decalin/ 1,3,5- trimethylbenzene (40/40/10/10)	39.94	1.63%	[13]
175.	n-dodecane/n-tetradecane/ isooctane/1,3,5-trimethylbenzene (12.9/47.9/75/10 Vol%)	23.89	2.64%	[13]
176.	n-dodecane/isooctane/ 1,3,5- trimethylbenzene (40/50/10 Vol%)	33.56	1.85%	[13]
177.	isooctane/1,3,5-trimethylbenzene (80/20 Vol%)	17.67	3.45%	[13]
178.	n-dodecane/ 1,3,5-trimethylbenzene (80/20 Vol%)	25.83	2.48%	[13]
179.	n-dodecane/decalin/ 1,3,5- trimethylbenzene (40/50/10 Vol%)	24.17	2.52%	[13]

180.	n-dodecane/n-tetradecane/1,3,5-trimethylbenzene (35/35/30 Vol%)	19.44	3.19%	[13]
181.	n-dodecane/ 1,3,5-trimethylbenzene (75/25 Vol%)	24.00	2.54%	[13]
182.	n-dodecane/n-tetradecane/ isooctane/decalin/1,3,5-trimethylbenzene (12.9/12.9/52.5/7.5/14.2 Vol%)	23.94	2.59%	[13]
183.	n-dodecane/n-tetradecane/ isooctane/decalin/1,3,5-trimethylbenzene (12.9/12.9/42.5/7.5/24.2 Vol%)	17.89	3.35%	[13]
184.	iso-cetane/ n-dodecane/1,3,5-trimethylbenzene) (52/23/25 mol%)	22.5		[14]
185.	iso-cetane/n-dodecane/methylnaphthalene (64/23/13 mol%)	24.2		[14]
186.	iso-octane/ n-dodecane/ 1,3,5-trimethylbenzene (54/18/28 mol%)	17.8		[14]
187.	toluene/n-heptane (42.6/57.4 mol%)	20.71995		[15]
188.	toluene/n-heptane/ naphthalene (41.04/55.29/3.67 mol%)	17.29939		[15]
189.	toluene/n-heptane/ tetralin (41.08/55.35/3.57 mol%)	18.3916		[15]
190.	toluene/n-heptane/ trans-decalin (41.16/55.45/3.39 mol%)	21.34086		[15]

191.	toluene/n-heptane/ cis-decalin (41.16/55.45/3.39 mol%)	21.34086		[15]
192.	n-Dodecane/Decalin/n-Butylbenzene/ Naphthalene (20.62/10.58/57.14/11.66 mol%)	8.7		[16]
193.	n-Dodecane/Decalin/n- Butylbenzene/Naphthalene (6.11/10.27/55.82/27.82 mol%)	6.5		[16]
194.	n-Dodecane/ Decalin/ n-Butylbenzene/ Naphthalene (0.43/10.84/49.54/39.20 mol%)	6.1		[16]
195.	n-Dodecane/Decalin/n- Butylbenzene/Naphthalene (36.16/51.81/9.41/2.62)	24.3		[16]
196.	n-Dodecane/Decalin/n-Butylbenzene (15.11/81.07/3.82/)	22.8		[16]
197.	n-Dodecane/Decalin/n-Butylbenzene (7.19/92.76/0.05 mol%)	22.1		[16]
198.	n-Dodecane/Decalin/n- Butylbenzene/Naphthalene (0.81/2.40/51.98/44.80 mol%)	5.5		[16]
199.	n-Dodecane/Decalin/n- Butylbenzene/Naphthalene (1.94/1.74/36.67/59.66 mol%)	5		[16]

200.	n-Dodecane/Decalin/n-Butylbenzene/Naphthalene (1.15/1.86/39.13/57.86 mol%)	5.3		[16]
201.	n-Dodecane/ Decalin/n-Butylbenzene/Naphthalene (0.61/2.13/63.78/33.48 mol%)	5.7		[16]
202.	n-Dodecane/ Decalin/ n-Butylbenzene/ Naphthalene (0.95/1.84/54.63/42.58 mol%)	5.7		[16]
203.	n-Dodecane/Decalin/n-Butylbenzene/Naphthalene (1.14/1.68/52.08/45.10 mol%)	5.5		[16]
204.	n-Dodecane/Decalin/n-Butylbenzene/ Naphthalene (73.77/11.45/10.47/4.31 mol%)	23.9		[16]
205.	n-Dodecane/Decalin/n-Butylbenzene/Naphthalene (73.93/7.25/14.51/4.31 mol%)	24.4		[16]
206.	diphenyl ether/gasoline (1/99 vol%)	15	3.33%	This work
207.	diphenyl ether/gasoline (5/95 vol%)	15	3.33%	This work
208.	diphenyl ether/ gasoline (10/90 vol%)	14.5	3.45%	This work

209.	diphenyl ether/gasoline (20/80 vol%)	9.5	5.26%	This work
210.	dioctyl ether/gasoline (1/99 vol%)	15.5	3.23%	This work
211.	dioctyl ether/gasoline (5/95 vol%)	16.5	3.03%	This work
212.	dioctyl ether/gasoline (10/90 vol%)	17.5	2.86%	This work
213.	dioctyl ether/gasoline (20/80 vol%)	24.5	2.04%	This work
214.	diethyl ether/gasoline (1/99 vol%)	15.5	3.23%	This work
215.	diethyl ether/gasoline (5/95 vol%)	18.5	2.70%	This work
216.	diethyl ether/gasoline (10/90 vol%)	22.5	2.22%	This work
217.	diethyl ether/gasoline (20/80 vol%)	25	2.00%	This work
218.	methyl tert-butyl ether/gasoline (1/99 vol%)	15.5	3.23%	This work
219.	methyl tert-butyl ether/gasoline (5/95 vol%)	17.5	2.86%	This work

220.	methyl tert-butyl ether/gasoline (10/90 vol%)	18.5	2.70%	This work
221.	methyl tert-butyl ether/gasoline (20/80 vol%)	19.5	2.56%	This work
222.	dibutyl ether/ gasoline (1/99 vol%)	20.5	2.44%	This work
223.	dibutyl ether/ gasoline (5/95 vol%)	25	2.00%	This work
224.	dibutyl ether/ gasoline (10/90 vol%)	28.5	1.75%	This work
225.	dibutyl ether/gasoline (20/80 vol%)	29.5	1.69%	This work
226.	diphenyl ether/diesel (1/99 vol%)	24.5	2.04%	This work
227.	diphenyl ether/ diesel (5/95 vol%)	19.5	2.56%	This work
228.	diphenyl ether/diesel (10/90 vol%)	17.5	2.86%	This work
229.	diphenyl ether/diesel (20/80 vol%)	16.5	3.03%	This work
230.	dioctyl ether/diesel (1/99 vol%)	19.5	2.56%	This work

231.	dioctyl ether/diesel (5/95 vol%)	24.5	2.04%	This work
232.	dioctyl ether/diesel (10/90 vol%)	25	2.00%	This work
233.	dioctyl ether/diesel (20/80 vol%)	29.5	1.69%	This work
234.	diethyl ether/diesel (1/99 vol%)	24.5	2.04%	This work
235.	diethyl ether/diesel (5/95 vol%)	25.5	1.96%	This work
236.	diethyl ether/diesel (10/90 vol%)	27	1.85%	This work
237.	20% diethyl ether+80% diesel (20/80 vol%)	30	1.67%	This work
238.	methyl tert-butyl ether/diesel (1/99 vol%)	19.5	2.56%	This work
239.	methyl tert-butyl ether/diesel (5/95 vol%)	23.5	2.13%	This work
240.	methyl tert-butyl ether/diesel (10/90 vol%)	25	2.00%	This work
241.	20%methyl tert-butyl ether+80% diesel (20/80 vol%)	26	1.92%	This work

242.	dibutyl ether/diesel (1/99 vol%)	20	2.50%	This work
243.	dibutyl ether/diesel (5/95 vol%)	23	2.17%	This work
244.	dibutyl ether/diesel (10/90 vol%)	27.5	1.82%	This work
245.	dibutyl ether/ diesel (20/80 vol%)	28	1.79%	This work

2.2.2 Determination of the functional groups

The molecular structure of the compound was used to determine the content of functional groups present. n-Heptane and 1-heptene are used as examples to demonstrate the calculation of the groups and BI. n-Heptane (MW = 100 g/mol) is made of two paraffinic CH₃ and five CH₂ groups (MW = 15 and 14 g/mol, respectively); thus, their total weights are 30 (2 × 15) and 70 (5 × 14) g/mol, respectively, and their proportions in n-heptane are 30 and 70 wt%, respectively. Consequently, the content of other functional groups is zero. Similarly, 1-heptene comprises one paraffinic CH₃, four paraffinic CH₂, and two olefinic CH=CH₂ groups at 15.3, 57.1, and 29.6 wt%, respectively. The BI determines the number of branched molecules by expressing the size and position of the branches of methyl/methylene in terms of numbers. Thus, the BI values of both groups that do not have a carbon atom connected to the longest carbon chain are zero. The distributions of the groups present in some neat compounds are depicted in Figure 6. To avoid over- or

under-representation, the weight proportion (wt%) was used instead of the mole proportion (mol%) to indicate the content of the functional groups [79].

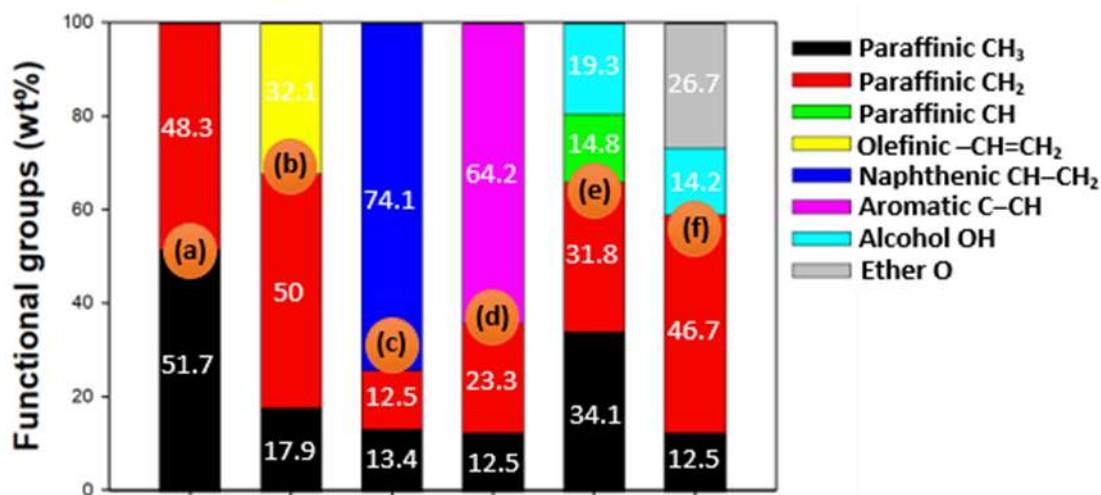


Fig. 4. Functional group distribution of some pure compounds: (a) *n*-butane, (b) 1-hexene, (c) ethyl cyclohexane, (d) propyl benzene, (e) 2-methyl 1-butanol, and (f) diethylene glycol methyl ether.

Generally, the volume fraction is used for representing and blending fuel. The functional groups of mixtures are determined using the densities and their blending ratios. The functional group distribution of some blends are reported in Figure 7. In the figure, the sum of the values of the functional groups of certain blends does not equate to 100%. This is because the quaternary carbon atoms in the paraffinic family was ignored in this study as their contribution is very low and they are difficult to quantify in petroleum fuels using ¹H NMR spectroscopy.

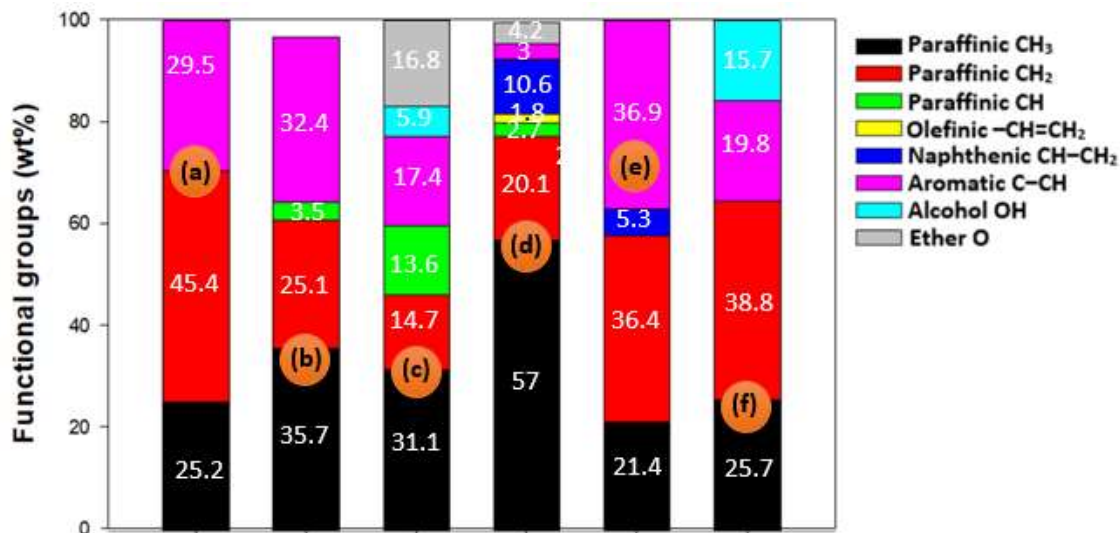


Fig. 5. Functional group distribution of sample blends. Compositions are expressed in vol% (a) 70% *n*-heptane–30% toluene, (b) 33.3% toluene–33.3% *iso*-octane–33.3% *n*-heptane, and (c) 70% TPGME (tripropylene glycol methyl ether) –30% TMB (1,2,4-trimethylbenzene), (d) 20% diethyl ether–80% gasoline (Vol%), (e) 10% tetralin –31.5 heptane–58.5 toluene, and (f) 70% 1-butanol – 30% 1,2,4 trimethylbenzene

MW is adopted as one of the 10 inputs provided to the proposed model because of the significant impact it has on the physical properties of fuels. The blend compositions are used for calculating the average MW of the blends. The average MWs of the eight gasoline and diesels were obtained using the procedure described in the literature [15]. The functional group and BI of gasoline and diesel were calculated from the ¹H NMR spectra and the methodology is described in detail [79].

2.2.3 ANN development

The data were randomly segregated into training (70%), validation (15%), and test (15%) sets. Training and validation were performed simultaneously. The validation was utilized for estimating the hyperparameters namely the number of hidden layers,

number of neurons, number of epochs, and loss function. The backpropagation tool was used to train the multilayer perceptron (MLP) for developing the ANN model. After training and validation, the test set was used for steering the ANN. The final assessment depended on the performance of the model after applying the test set. The parameter optimization was performed using the NN tool in the MATLAB environment. The models were evaluated through fine controlling by exclusively using the validation set, after which the test set was employed. The considered hyperparameters were optimized by determining the minimum error for a certain ANN via numerous iterations (epochs). The epoch refers to the number of patterns used (each compound or mixture has one pattern). The optimized parameters (best parameters) were used in the final model. After determining the optimal topology, the ANN model was retrained, validated, and tested using the corresponding test sets.

Herein, the datasets comprising 366 training points, have 10 inputs and one output (SP) for each point. Pearson correlation's analysis presented in Figure 8 shows the correlation between each input and the SP. In the figure, two inputs, namely, the aromatic C–CH group and BI, numerically exert the most effect on the SP, whereas the alcoholic OH group exerts the lowest effect. However, because the correlations between the 10 inputs and the one output are nonlinear, as shown in the results and discussion section below, the combination of insignificant inputs may afford significant findings.

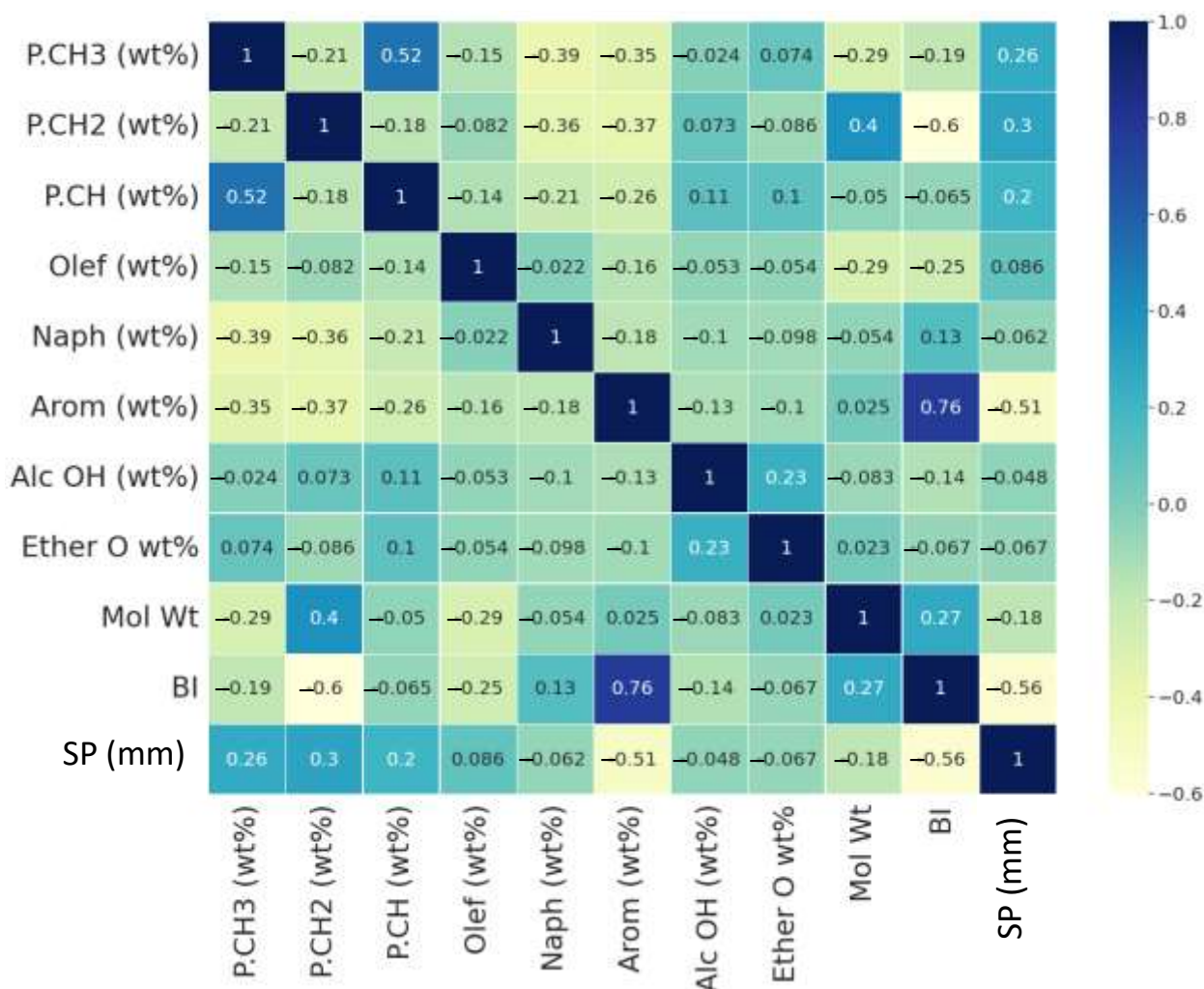


Fig. 6. Input and output features are represented using Pearson's correlation.

Because the ranges of the hyperparameters are very large, the parameters must be analyzed separately to reduce computational costs. This indicates that varying a single parameter solely can yield suboptimal results; therefore, some differences in the remaining parameters are retained for including their correlation. As an example, if the number of hidden layers is targeted, the obtained result will be the average of a subset of the numbers of hidden neurons and epochs that are tested. As and when the hyperparameters are determined, the subsequent levels are fixed until all the parameters are finalized. In the

present work, the parameter mean absolute error was used as the loss function to judge the accuracy of the model.

2.3 Results and Discussions

The molecular structure of compounds and mixtures determines their SPs. In this section, we separately discuss the effect of the 10 inputs (features) on the SP. Generally, all the relations between the 10 inputs and the output (either pure compounds (a) or mixtures (b)) are mostly nonlinear (Figures 7–16). Therefore, we employed the ANN model to improve the prediction of the SP of the fuels. The nonlinear relation between the inputs and the output is described below.

2.3.1 Paraffinic CH₃ groups

Overall, paraffins exhibit higher-intensity flames than the other classes of hydrocarbons such as olefins and naphthenes. Thus, the SPs of paraffins are higher than those of the other types of hydrocarbons. This is demonstrated by *n*-hexane, which shows a SP of 149 mm. This is the highest value compared to the other six carbon groups: 1-hexene, cyclohexene, and benzene (SP = 55.2, 38.7, and 8.79 mm, respectively). The effect of paraffinic CH₃ groups on the SP of neat compounds and various blends is shown in Figure 9. In the figure, the SP of paraffins, which contain a straight chain, increases with the increasing mass of the paraffinic CH₃ groups. Ethane, comprising 100% paraffinic CH₃, achieves the highest SP of 319 mm (as experimentally determined in the literature [45]) among the fuels in the dataset. The SP (163 mm) of *n*-pentane (41.67% CH₃) is higher than those of hexane (149 mm; 39.88% CH₃) and *n*-heptane (139 mm; 30% CH₃). The *iso*-paraffins containing eight carbon atoms: 3-methyl heptane (39.47% CH₃), 2,2-dimethyl hexane (52.63% CH₃), and 2,3,4-trimethylpentane (65.79% CH₃) contain 3, 4, and 5 CH₃

groups, respectively; the SPs of these hydrocarbons are 120, 87.3, and 59 mm, respectively. These SP values appear to decrease with increasing CH₃ content. This trend is also observed in other *iso*-paraffins. Paraffins with numerous branches exhibit lower SPs than those with fewer branches but the same number of carbon atoms. For example, *n*-octane achieves a higher SP (137 mm) than 2-methyl heptane (102 mm) and 2,2-dimethyl hexane (87.3 mm). This behavior is observed for all paraffins with the same number of carbon atoms. The addition of a methyl group to an aromatic ring reduces the SP value owing to the addition of the three H atoms which can stabilize the benzyl group formed via H abstraction, followed by ring addition, subsequently affording polyaromatic hydrocarbon (PAH) species. In other types of hydrocarbons, an inconspicuous trend is observed because the SP is dependent on the CH₃ groups as well as the net effect of the total functional groups forming the compounds.

The gasoline samples and their surrogates may show the highest mass contribution of paraffinic CH₃ groups [15] compared to most classes of petroleum fuels. The effect of paraffinic CH₃ groups on the blends present in the current dataset is depicted in Figure 7b. The SPs of mixtures comprising the compounds (*iso*-octane–toluene, 2,2,4,4,6,8,8-Heptamethylnonane (HMN)–TMB, methylcyclohexane (MCH)–1-methylnaphthalene(1-MN), decalin–1-MN, 1-MN–TMB, *n*-heptane–toluene, naphthalene–*n*-heptane–toluene, *n*-octane–*n*-heptane–toluene, 1-butanol–*n*-hexadecane (HD)–TMB, and tetralin–*n*-heptane–toluene) increase with increasing CH₃ content, whereas the opposing trend is observed in the remaining mixtures (*m*-xylene–*n*-dodecane, HD–TMB, and TPGME–TMB) because of the significant impact of other functional groups. For example, the SP of decalin-1-MN decreases drastically when the content of

MCH is increased, although changes in the methyl group of the mixtures is low. This is attributed to the decrease in the content of aromatic groups, which significantly affects the SP more than the methyl group. Error bars from the source are added to the data points in the following figures.

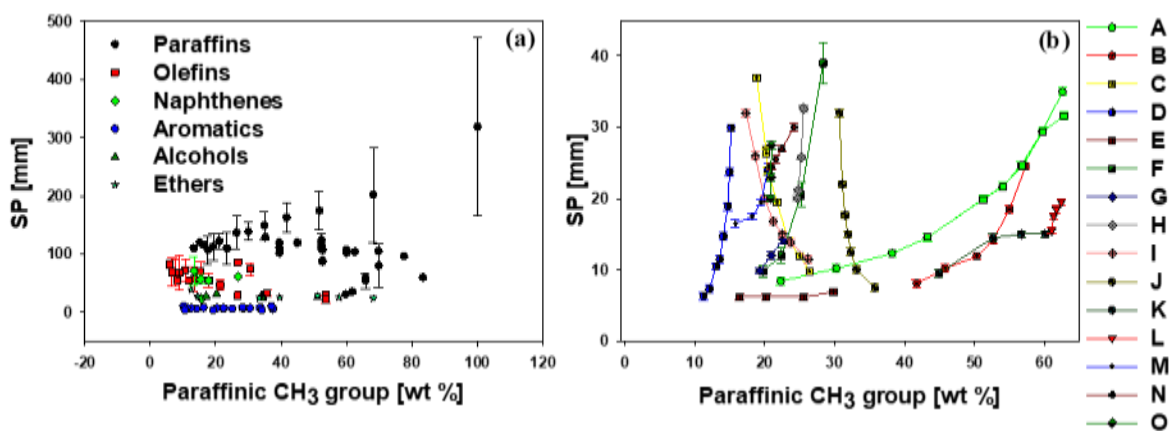


Fig. 7: Effect of paraffinic CH₃ groups on SPs of (a) pure compounds and (b) blends (*iso*-octane–toluene (A); HMN–TMB (B); *m*-xylene–*n*-dodecane (C); MCH–1-MN (D); TMB–1-MN (E); *n*-heptane–toluene (F); naphthalene– *n*-heptane–toluene (G); *n*-octane–*n*-heptane–toluene (H); HD–TMB (I); TPGME–TMB (J); diphenyl ether–gasoline (K); methyl tert-butyl ether (MTBE)– gasoline (L); diphenyl ether–diesel (M); diethyl ether–gasoline(N) and dibutyl ether–diesel (O)).

2.3.2 Paraffinic CH₂ groups

The contents of the methyl and methylene (CH₂) groups considerably affect paraffin combustion behavior [80]. Furthermore, a similar ignition delay has been experimentally observed for the mixtures of paraffinic fuels with a similar CH₂/CH₃ ratio [81]. The paraffinic CH₂ groups can be used to determine the molecule linearity, as

described in the literature [79, 82], where a high methylene content denotes a high level of linearity in branched paraffins, which show lower sooting tendencies than their straight-chain counterparts [83]. Figure 10 shows the impact of the paraffinic CH_2 group on the SPs of the pure compounds and the blends. The SP of n-paraffins tends to decrease with the number of carbon atoms, indicating that the content of paraffinic CH_2 negatively correlates with the SP. This may also be due to increase in the size of the molecular, yielding enhanced sooting tendencies [84]. The SP also decreases when the number/length of the paraffinic chains linked to the aromatic rings increases, due to the reaction between the benzene group and HC radicals formed by chain decomposition [85]. The formation of the soot precursors of naphthalenes and other polyaromatics also follows this mechanism. The significant variations in the SP of alkyl aromatics (either primary or secondary and tertiary) are attributed to the variation in the growth pathways and sooting tendency [85].

From the Figure 8b it can be observed that SP has a linear correlation with the methylene groups in most of the observed blends where increasing CH_2 groups tends to increase the SP. This opposing trend can be explained with the blends of dibutyl ether/dioctyl ether with gasoline/ diesel. Addition of the aforesaid ether compounds results in the net increase of the CH_2 groups in the blend. While at the same time, the net reduction of the aromatic groups in the blend is larger, which causes an increase in the SP (and a reduction in soot). An increase in the percentage of diphenyl ether in the gasoline blends lead to a increase in aromatic groups and decrease of CH_2 groups causing a reduction in the SP. The same behavior was noted when the diphenyl ether was blended with diesel.

In MTBE–gasoline and MTBE–diesel blends, increasing the blend ratio of MTBE resulted in downfall of SP due to the fall in the aromatic groups present in the petroleum fuels.

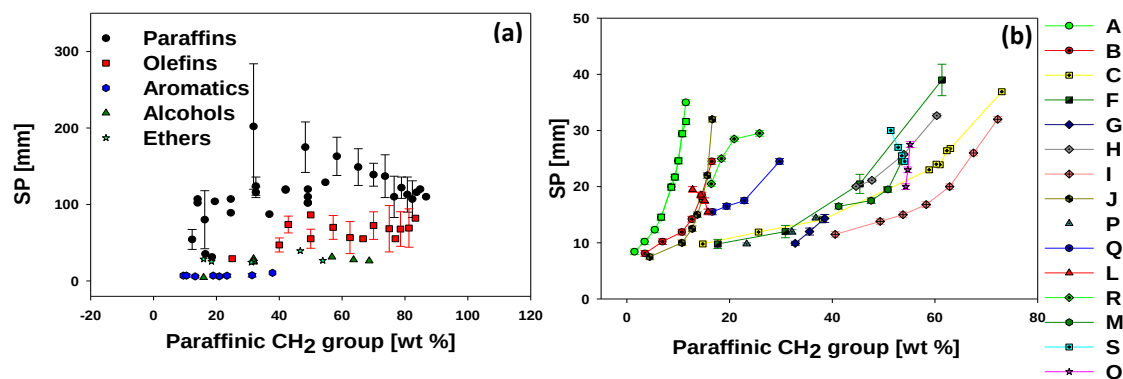


Fig. 8. Effect of paraffinic CH₂ groups on SPs of (a) pure compounds and (b) blends (*iso*-octane–toluene (A); HMN–TMB (B); *m*-xylene–*n*-dodecane (C); *n*-heptane–toluene (F); naphthene– *n*-heptane–toluene (G); *n*-octane–*n*-heptane–toluene(H); HD–TMB (I); TPGME–TMB (J); benzene–heptane–toluene(P); dioctyl ether–gasoline (Q); MTBE–gasoline (L); dibutyl ether–gasoline (R); diphenyl ether–diesel (M); diethyl ether–diesel (S) and dibutyl ether–diesel (O)).

2.3.3 Paraffinic CH groups

The SP of branched paraffins decreases when the content of paraffinic CH increases. For example, 2-methyl pentane (15.9% CH) shows a higher SP (116 mm) than 2,3-dimethyl butane (105 mm; 30.23% CH). As another example, the SP (119 mm) of 2-methyl hexane (13% CH) is higher than that of 2,4-dimethylpentane (102 mm; 26% CH). This is because 2,4-dimethyl pentane has two CH groups and the above behavior is typical for *iso*-paraffins with the same number of carbon atoms. From Figure 11, it can be seen

that the SPs of three blends namely *iso*-octane–toluene, HMN–TMB, and TPGME–TMB increase with increasing content of paraffinic CH groups. This is because the total content of aromatic groups in the mixtures decreases as the content of paraffinic groups increases. Therefore, the content of aromatics exerts a higher effect on the SP of blends than the content of CH groups. This is consistent with the measurement trend of the ignition delay of *iso*-octane–toluene and *n*-heptane–*iso*-octane–toluene blends where the impact of the paraffinic CH group is less pronounced than that of the aromatic groups [47].

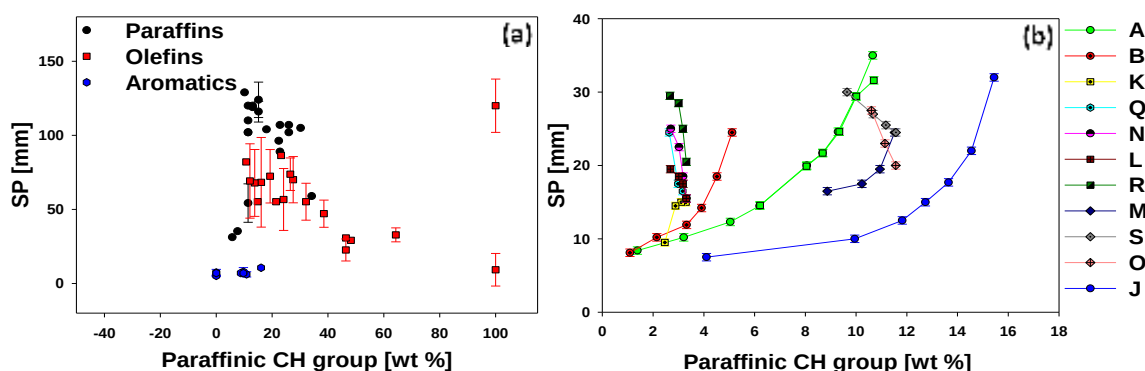


Fig. 9. Effect of paraffinic CH groups on SPs of (a) pure compounds and (b) blends (*iso*-octane–toluene (A); HMN–TMB (B); diphenyl ether–gasoline (K); dioctyl ether–gasoline (Q); diethyl ether–gasoline (N); MTBE– gasoline (L); dibutyl ether–gasoline (R); diphenyl ether–diesel (M); diethyl ether–diesel (S); dibutyl ether–diesel (O) and TPGME–TMB (J))

2.3.4 Olefinic –CH=CH₂ groups

The olefinic –CH=CH₂ groups significantly affect the autoignition behavior and oxidative stability of fuels. Gasoline and diesel contain a lower content of olefinic groups than other hydrocarbon groups. Generally, olefins show a higher sooting tendency (a low flame height corresponds to a low SP) than their *n*-paraffin and *i*-paraffin counterparts. For

example, the SPs of 1-pentene (47.1 mm) and 1-octene (56.7 mm) are lower than those of *n*-pentane (163 mm) and *n*-octane (137 mm). The impact of the olefinic –groups on the SP is shown in Figure 12. The olefinic double bonds present in cycloparaffins tend to promote soot formation due to their higher impact on the sooting tendency than methyl substitutions [81].

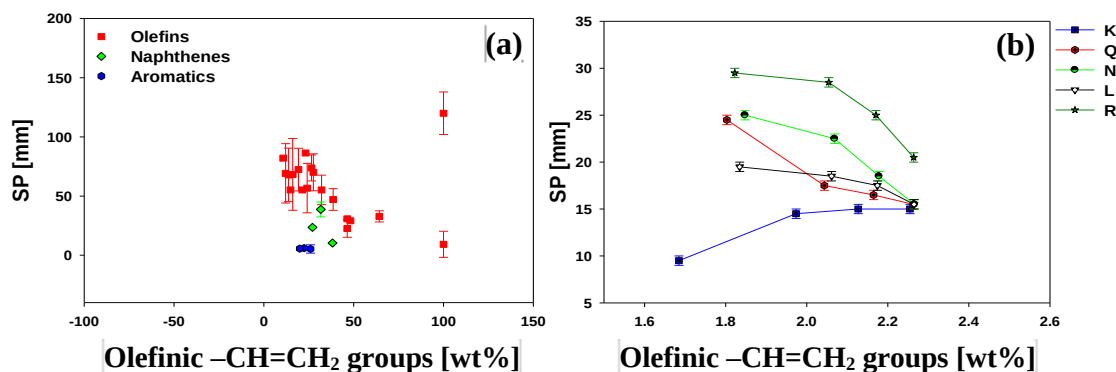


Fig. 10. Effect of olefinic –CH=CH₂ groups on SPs of (a) pure compounds and (b) blends (diphenyl ether–gasoline (K), dioctyl ether–gasoline (Q), diethyl ether–gasoline (N), MTBE–gasoline (L), and dibutyl ether–gasoline (R)).

2.3.5 Naphthenic –CH–CH₂ groups

Naphthenes generally exhibit lower SPs compared to other hydrocarbons of similar size. Adding cyclic fuels containing unsaturated double bonds promotes soot inception as experimentally observed in *n*-heptane flames [81]. Furthermore, the doping of cyclic fuels with *n*-heptane increases the size and quantity of the soot particles, which was experimentally determined at a low flame height [81]. Figure 13 shows the effect of the naphthenic groups. The increase in the content of the naphthenic groups decreases the SP

of the tetralin–*n*-heptane–toluene blend but increases the SP of the MCH–1-MN and decalin–1-MN blends. This is because the content of aromatics is reduced by the addition of MCH, indicating that aromatics exert a higher effect on the SP than naphthenes.

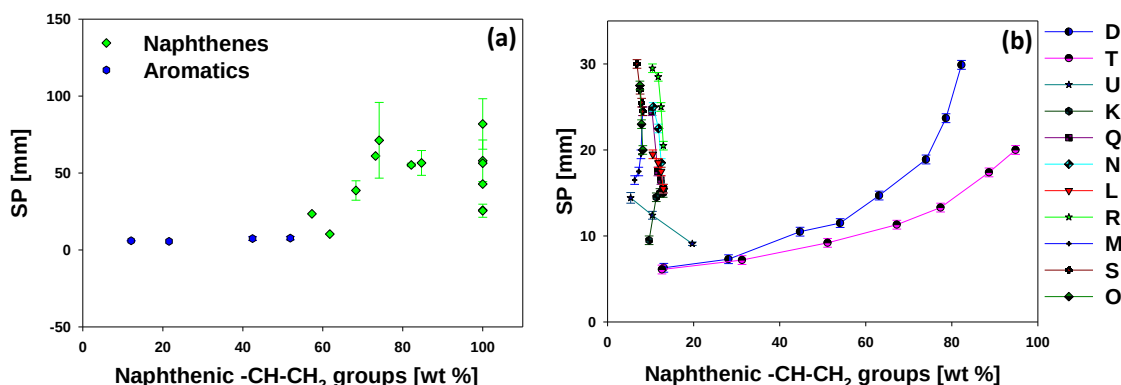


Fig. 11. Effect of naphthenic $-\text{CH}-\text{CH}_2$ groups (wt%) on SPs of (a) pure compounds and (b) blends (MCH–1-MN (D), decalin-1-MN (T), tetralin-*n*-heptane-toluene (U), diphenyl ether–gasoline (K), dioctyl ether–gasoline (Q), diethyl ether–gasoline (N), MTBE–gasoline (L), dibutyl ether–gasoline (R), diphenyl ether–diesel (M), diethyl ether–diesel (S) and dibutyl ether–diesel (O)).

2.3.6 Aromatic C–CH groups

The content of aromatics in fuels (gasoline, diesel, and jet fuels) varies depending on three factors: the target application, refining practices, and the parent crude. Petroleum fuels contain various aromatic compounds such as benzene, xylene, toluene, naphthalene, and alkylbenzene [86]. Several studies have demonstrated [85, 87–89] the significant impact of aromatics on overall fuel properties, which are important

contributors to soot formation. The flame produced by aromatic fuels emits PAHs at high concentrations. This is also observed at a low flame height. In the post-oxidation zone, the soot precursors quantitatively increase because of dehydrogenation, followed by ring addition/formation [90]. Figure 14 shows the relation between the SPs of pure compounds/ blends and those of aromatic groups. The SPs consistently decrease with increasing content of aromatic groups for most of the blends, conforming to the aforementioned results. The aromatic C–CH groups negatively affect the SPs of compounds and the blends more than the other group mentioned in this work. For example, adding diphenyl ether at 1, 5, 10 and 20% to diesel, results in 6, 10, 17 and 25 wt% of aromatics groups in the blends, respectively. This consequently results in decreasing SPs of 24.5, 19.5, 17.5 and 16.5 mm respectively. On the other hand, for dibutyl ether–diesel blends, addition of dibutyl ether at 1, 5, 10 and 20% results in mixture SPs of 20, 23, 27.5 and 28 mm due to decreasing aromatic groups in the mixture.

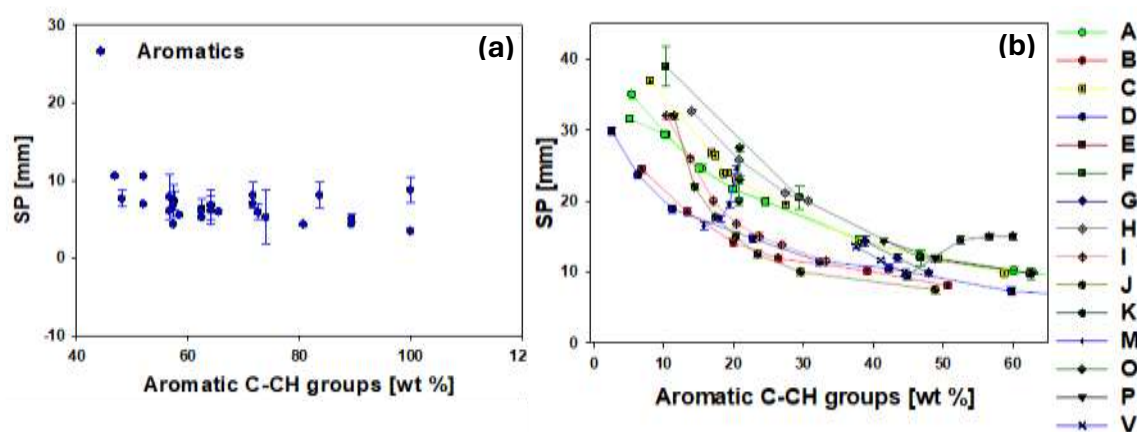


Fig. 12. Effect of aromatic C–CH groups (wt%) on SPs of (a) pure compounds and (b) blends (iso-octane–toluene (A); HMN–TMB (B); m-xylene–dodecane (C); MCH–1-MN (D); TMB–1-MN (E); n-heptane–toluene (F); naphthene– n-heptane–toluene (G); n-octane–n-heptane–

toluene (H); HD-TMB (I); TPGME-TMB (J); diphenyl ether-gasoline (K); diphenyl ether-diesel (M); dibutyl ether-diesel (O); benzene-*n*-heptane-toluene (P) and 1-MN-*n*-heptane-toluene (V)).

2.3.7 Alcoholic OH groups

When alcohols are added to petroleum fuels, the hydroxyl OH radicals acts as a scavenger, decreasing both the low temperature heat release and fuel reactivity [91]. The combustion efficiency of petroleum fuels can be increased by adding alcohol compounds like ethanol that carries an oxygen atom in the fuel leading to better oxidation. Generally, gasoline is blended with alcohols—such as ethanol—to act as an octane booster. The ethanolic OH group significantly contributes to the increase in gasoline octane rating compared to other hydrocarbon functional groups [16]. The SPs of primary alcohols are generally higher than those of olefins with the same numbers of carbon atoms. For example, the SPs of 1-butanol and 1-butene are 31.3 and 29.1 mm, respectively. Notably, 1-butanol exhibits the highest SP (31.3 mm) among the alcohols in the dataset because it contains a higher OH content (22.97 wt%) compared to other five carbon alcohols. Secondary alcohols exhibit lower SPs than both primary alcohols and *n*-paraffins with the same size. Figure 15 presents the impact of the alcoholic OH groups on the SP, from where it can be seen that the SPs of the blends increases as the OH groups increase. Alternatively, the opposing behavior is seen for the case of TPGME-HD-TMB blend. This is because the content of aromatic groups, which exerts a more significant effect, as mentioned previously, increases with the increasing content of the OH groups.

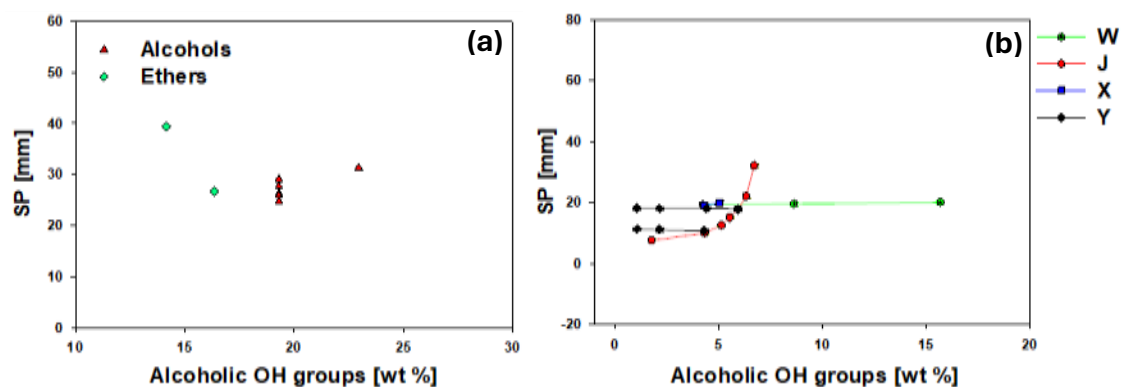


Fig. 13. Effect of alcoholic OH groups (wt%) on SPs of (a) pure compounds and (b) blends (1-butanol–HD–TMB (W); TPGME–TMB (J); 1-undecanol–HD–TMB (X) and TPGME–HD-TMB (Y)).

2.3.8 Ether O groups

Applying the same rules used in the case of paraffins, studies have been conducted on the oxidation reaction of ether [92-94]. Ether molecules show the highest SP among hydrocarbon and alcohol molecules of the same size. The continuity of a carbon chain can be broken by the oxygen atom in an ether molecule, affording smaller species. These species are better oxidized, and consequently, few PAHs (soot precursors) are likely formed. Several ether compounds—such as diethyl ether, dimethoxymethane, and polyoxymethylene—have been employed as diesel additives to hinder soot formation under fuel-rich conditions. Recently, it was observed that the premixed laminar flame of dimethyl ether did not induce soot formation [95]. This is attributed to the lack of C–C bonds in the compound. The mixture of dimethyl ether and acetylene (acting as soot precursors) affords soot at small contents with an equalized ratio of 1. When this ratio is increased, the content of soot formed tends to increase. However, the soot content decreases with increasing dimethyl ether ratio in the mixture.

The impact of the ether O groups on the SP of pure compounds and mixtures is shown in Figure 16. Some pure ethers have higher SPs compared to the other hydrocarbons classes mentioned here. For example, the ethers (diphenyl ether, dioctyl ether, diethyl ether) have SPs of > 50 mm. This explains the need for using ethers for blending with gasoline or diesel. The average trend of shown in Figure 14a appears to show an increase the SPs of pure ethers as the content of ether O groups increases. For example, diphenyl ether, ethylene glycol monopropyl ether, sec-butyl methyl ether and diethylene glycol methyl ether having ether contents of 9.41, 15.38, 18.18 and 26.67%, respectively, show increasing SPs of 5, 26.7, 28.5 and 39.4 mm, respectively. For the mixtures, the results showed that the SPs of the blends of gasoline and diesel with ethers (diethyl ether, dibutyl ether, dioctyl ether, and MTBE) increased as the content of the ether O groups increased. Thus, by increasing the ether content in the blend, the SP increases. For example, mixing the gasoline with 1%, 5%, 10%, and 20% dibutyl ether increased the SP of gasoline from 15 ± 0.5 to 20.5 ± 0.5 , 25 ± 0.5 , 28.5 ± 0.5 , and 29.5 ± 0.5 mm, respectively. The opposite trend was observed in the case of blends of diphenyl ether with gasoline and diesel. For instance, mixing the diesel with 1%, 5%, 10%, and 20% diphenyl ether decreased the SP of diesel from 29.5 ± 0.5 to 24.5 ± 0.5 , 19.5 ± 0.5 , 17.5 ± 0.5 , and 16.5 ± 0.5 mm, respectively (as shown in Figure 4 for the last data). This is because the aromatic groups exert more negative effects on the sooting tendency than other groups. An increase in the content of diphenyl ether increased the content of aromatic groups in the blends, which decreased their SPs. The SPs of the TPGME–HD–TMB blend show an almost horizontal trend which is due to similar content of aromatic groups in all the blends.

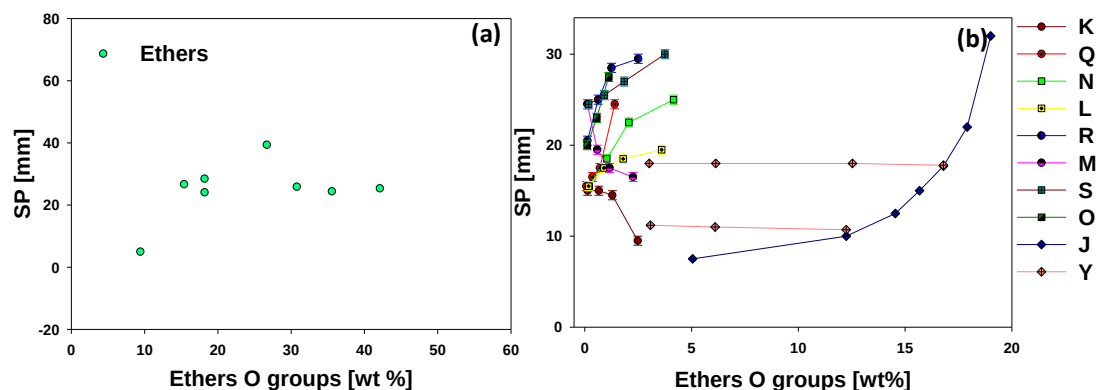


Fig. 14. Effect of ether O groups (wt%) on SPs of (a) pure compounds and (b) blends (diphenyl ether–gasoline (K); dioctyl ether–gasoline (Q); diethyl ether–gasoline (N); MTBE–gasoline (L); dibutyl ether–gasoline (R); diphenyl ether–diesel (M); diethyl ether–diesel (S); dibutyl ether–diesel (O); TPGME–TMB (J) and TPGME–HD–TMB (Y)).

2.3.9 Molecular weight

Generally, the SP of all types of hydrocarbons/ oxygenated compounds decreases with increasing MW. The soot produced by C_{16} fuels is higher than that produced by C_7 fuel [84]. However, the maximum soot produced considerably depends on the initial aromatic rings of the tested fuel [96]. Experimental observations have shown that the soot-formation tendency of the *n*-decane–HD blend used in diesel engines increases with the MW of the fuel mixtures [96]. Moreover, the soot volume fraction from a gas turbine and jet flame fueled with blends of paraffins (*n*-heptane, *n*-dodecane, and HD) increases with increasing MW of the fuel mixtures for two types of flames (non-premixed and premixed) [84]. Figure 17 shows the effect of MW on the SP of the compounds and blends. The SPs of *n*-paraffins dramatically decreases with an increasing number of carbon atoms, whereas

those of *iso*-paraffins decrease with a decrease in the number of carbon atoms provided the extent of branching remains similar. This behavior is observed in all the classes of compounds. The SPs of some aromatic containing blends namely TPGME–TMB (J), HD–TMB (I) and *n*-octane–*n*-heptane–toluene (H); increases with an increase in the MW due to the reduction in aromatic groups. This again shows the dominance of the aromatic functional groups on SP.

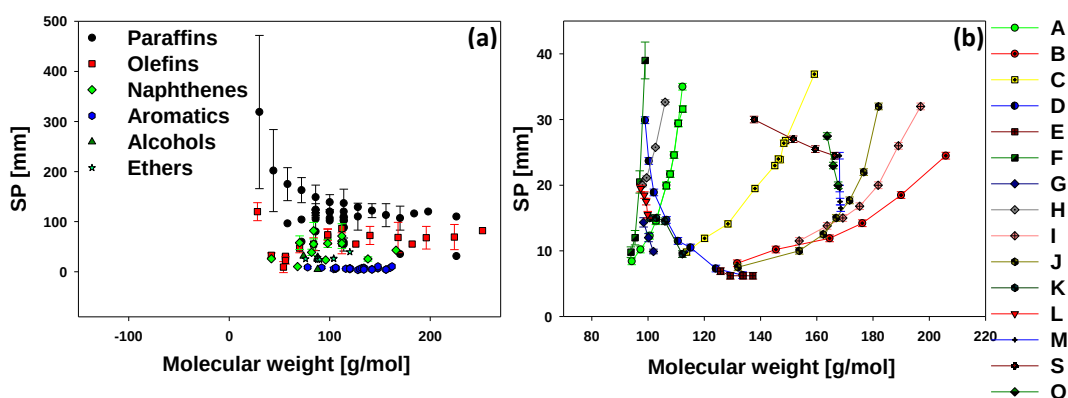


Fig. 15. Effect of MW on SPs of (a) pure compounds and (b) blends (*iso*-octane–toluene (A); HMN–TMB (B); *m*-xylene–dodecane (C); MCH–1-MN (D); TMB–1-MN (E); *n*-heptane–toluene (F); naphthalene–*n*-heptane–toluene (G); *n*-octane–*n*-heptane–toluene (H); HD–TMB (I); TPGME–TMB (J); diphenyl ether–gasoline (K); MTBE– gasoline (L); diphenyl ether–diesel (M); diethyl ether–diesel (S) and dibutyl ether–diesel (O)).

2.3.10 Branching index (BI)

Several studies [16, 58, 64, 79, 97-101] have reported the influence of degree of branching on fuel characteristics. The physical, chemical and combustion properties of compounds are significantly affected by the branching and also by the position of the alkyl

branch on the carbon chain. For instance, although 2-methyl heptane (SP = 120 mm), 3-methyl heptane (SP = 110 mm), and 4-methyl heptane (SP = 102 mm) show the same number and distribution of functional groups, their SPs vary depending on the branching position on the carbon chain. Abdul Jameel et al. [79] reported that the BI can be used for determining the impact of branching on the property of the compound by considering the branching position. The BI of n-paraffins is defined as zero. In addition to the BI of i-paraffins, the BI of ring structures connected to side chains has been calculated [79]. The BIs of n-hexane, 2-methyl hexane, and 3-methyl hexane are 0, 0.17, and 0.25, respectively. These values can explain the variation in their SPs, as noted previously. The higher the BI value, the greater the extent of branching present in the compound. Figure 18 presents the effect of BI on the SP of the pure compounds and blends. This figure shows that the SPs decrease as the BIs increase. This behavior is clearly observed in all the pure compounds and blends considered in this study.

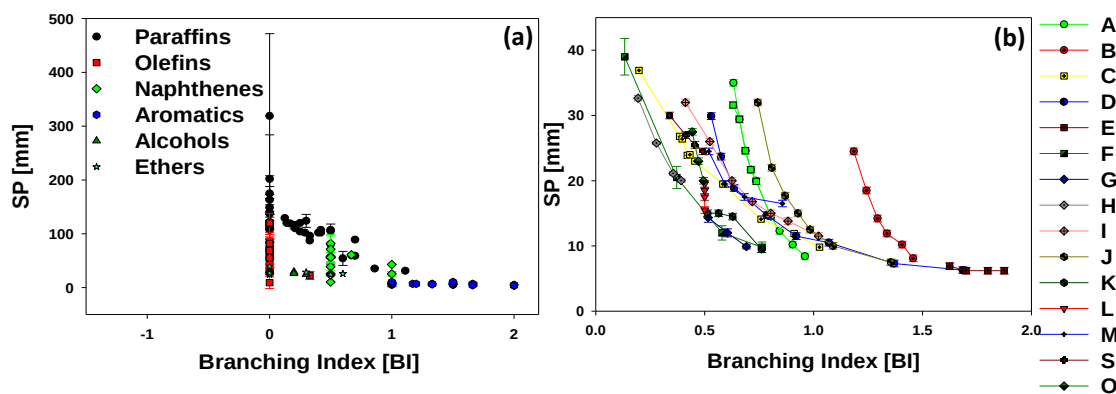


Fig. 16. Effect of BI on SPs of (a) pure compounds and (b) blends (*iso*-octane–toluene (A), HMN–TMB (B); *m*-xylene–dodecane (C); MCH–1-MN (D); TMB–1-MN (E); *n*-heptane–toluene (F); naphthene–*n*-heptane–toluene (G); *n*-octane–*n*-heptane–toluene

(H); HD–TMB (I); TPGME–TMB (J); diphenyl ether–gasoline (K); MTBE– gasoline (L); diphenyl ether–diesel (M); diethyl ether–diesel (S) and dibutyl ether–diesel (O)).

2.3.11 ANN model

The final ANN model generated by abovementioned strategy was employed to predict the SP based on the 10 inputs. The best hyperparameters obtained by continuous optimization of the neural network topology are listed in Table 1.

Table 3: Optimized hyperparameters of the final model

Parameter	Description
Hidden layers	1
Neurons	10
Epochs	317

To analyze the prediction accuracy of the developed ANN model, the test set containing 15% of the data was employed to calculate the mean of the predicted SPs. This test set was not used for the training or fine-tuning of the model. The test set was automatically selected using an inbuilt algorithm within Matlab and was used as a criterion to check the performance of the final model. The model performance was evaluated by plotting the measured and predicted SPs using the test set (Figure 19), achieving an R^2 of 0.98, indicating a good correlation between the measured and predicated SPs. Therefore, the generated model with functional groups as inputs can be employed to predict the SP of compounds and petroleum fuels containing oxygenate additives. The good performance of this model is attributed to the use of advanced tools, such as the ANN. One of the most

important novelties of this modeling strategy and the reason for its predictive capability is that no two fuels in the dataset that have the same SP, also possess similar functional group distribution. This indicates the innate ability of the modeling approach to quantify fuels from their constituent functional groups as a useful criterion. In the present study, the mean absolute error obtained was 4.5, which is close to the uncertainty accompanying experimental SP measurements. The SP prediction model is uploaded on the GitHub repository (<https://github.com/mohammed-Qasem/Smoke-Point-SP-Model.git>).

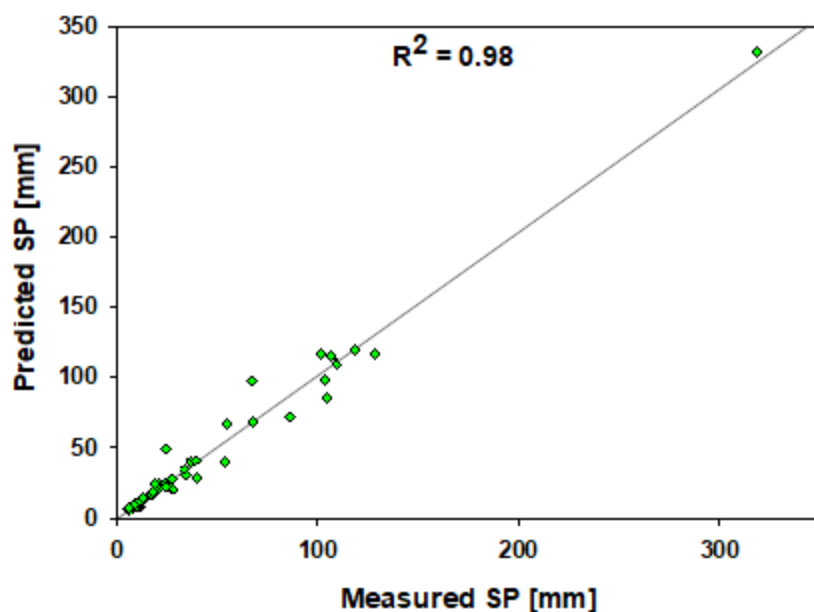


Fig. 17. Comparison between the predicted and measured SPs.

2.4 Conclusions

Herein, an AI-based ANN model was developed using machine learning by employing a dataset of 366 fuel samples comprising 37 paraffins, 19 olefins, 13 naphthene, 30

aromatics, 6 alcohols, 8 ethers, 245 fuel blends, 8 types of gasoline and diesel samples to predict the SPs of hydrocarbons, mixtures, and real fuels. The most significant correlations between the inputs and the output of the ANN model were between the SP as well as aromatic groups and the BI, as determined using Pearson's correlation. This observation was supported by the trends of the fuel mixtures. The final ANN model comprises a hidden layer containing 10 neurons. This model was established after running 317 epochs using the 70% training set. Thereafter, the model was validated using the 15% validation set. The correlation between the experimental and predicted SPs was positive ($R^2 = 0.98$). The mean absolute error was 4.5, which is considerably preferred over the uncertainty of the experimentally measured SP. The generated SP model can be employed for predicting the SP of neat compounds, surrogates, and real fuels if their constituent functional groups are known.

Chapter 3:

A machine learning model for predicting threshold sooting index (TSI) of fuels containing alcohols and ethers.

Particulate matter (PM) emissions like soot are a byproduct of the combustion of fossil fuels at various point sources [102]. For example, PM emitted from the aviation industry has led to pollution in the atmosphere of airports and its vicinities. Similarly, combustion of gasoline and diesel fuels in internal combustion (IC) engines for land-based transportation has drastically affected the air quality, both in urban and semi-urban areas. PM emissions from carbon-based fuels have been linked with ecological problems like floods, climate change, tsunamis and even drought [103, 104]. Inhalation of PM has also caused negative health effects like respiratory problems, skin irritation, cancer, and more.

Several methods have been used to measure the sooting propensity of fuels like micro pyrolysis index [105], TSI [106], yield sooting index [85] and OESi [107]. Amongst these, TSI proposed by Manos and Calcote [45], has been extensively used and reported in the literature owing to the low fuel requirements, low cost, simple implementation and experimental requirements. TSI is a parameter that quantifies the sooting propensity of fuels. It is calculated from the measured SP of the fuel using Eq. (1), given below.

$$TSI = a \frac{MW}{SP} + b \quad (3.1)$$

where SP is the maximum height (in mm) attained by a smokeless diffusion flame produced by a standard wick lamp operated at specified standard conditions. MW refers to the molecular weight of the fuel (in g/mol) and the terms ‘a’ and ‘b’ are calibration constants specific to the equipment. The sooting propensity of a large number of fuels

including petroleum fuels [15], pure compounds [33, 45, 67, 76, 78, 108-110] and their mixtures [15, 30, 34, 67-75, 78, 111-115] have been evaluated using TSI.

An effective way to reduce soot formation observed in engine exhausts is by blending petroleum fuels with select oxygenated additives derived from renewable sources like biomass [51-53] which have low sooting propensities [30, 51-53, 55-57]. In this regard, alcohols [91] and ethers [55, 56, 116, 117] have been shown to be very promising in reducing the soot emissions. The oxygen content in these additives enables better oxidation of the hydrocarbon radical pool thereby decreasing the formation of soot precursors. The reduction of soot is also dependent on the molecular structure of the additives along with the oxygen content. Alcohols and ethers also produce lesser NO_x and CO emissions compared to conventional gasolines [59]. Though these oxygenated fuels can operate IC engines in their pure forms, their application is limited due to the various issues like low energy density, corrosiveness, and poor lubricating features [16]. As a result, alcohol and ether compounds are routinely blended with petroleum fuels to improve their properties [58]. Refineries are constantly in the process of exploring new oxygenated molecules that reduce soot formation whilst possessing high energy density. Experimentally measuring TSI of large number of fuels can be time consuming and therefore, there is a need for mathematical models that can predict the TSI especially, when there is a need to screen a large number of new fuel compositions.

The objective of this investigation is to develop a mathematical model for predicting TSI of neat compounds, fuel surrogate mixtures and petroleum fuels containing alcohol and ether functionalities. Since TSI is measured using a standard SP lamp operated at standard conditions [118], the measured property (TSI) is solely a function of the fuel's

molecular structure/chemical composition. Therefore, it is integral when developing a TSI prediction model to use the fuel's molecular information, which can be expressed in the form of functional groups as shown by a number of works [15, 16, 63, 64, 79, 119-122]. The functional groups present in a molecule/mixture determines its properties such as sooting propensities [61], cetane number [79, 98], octane number [16], flash point [24], ignition delay [63], and auto-ignition [62], etc. Several studies [27, 33, 64, 80, 121, 123-125] have reported that a fuel's functional groups can reproduce their physical, chemical and combustion behavior. Oxygenated fuels possessing alcohol and ethers can be separated into eight functionalities namely, paraffinic CH₃, paraffinic CH₂, paraffinic CH, naphthenic CH-CH₂, olefinic -CH=CH₂, aromatic C-CH, alcohol OH and ether O groups which can serve as inputs for developing a TSI model. Another two molecular parameters, molecular weight and branching index (BI) have also been shown to affect fuel physical properties like density, viscosity, vaporization etc. and therefore is included as inputs to the model in addition to the eight functional groups.

One of the objectives of the model is the accurate prediction of TSI of fuel surrogate mixtures. A linear mixing rule dependent on the mole fractions of the mixture species, developed by Olson et al. [76] has been used for predicting the TSI of mixtures. Several studies [126-128] have used the linear by mole mixing rule for predicting the TSI of hydrocarbon mixtures. However, this rule is limited in its accuracy especially when applied to ternary mixtures and above. Yan et al. [32] reported a parabolic curve for TSI of toluene/n-octane mixtures and showed large errors when linear by mole rules were used to predict the TSI of paraffin-aromatic mixtures. Similar errors have been shown by Haas et al. [37] when linear mixing rules were applied for TSI for binary mixtures (e.g. iso-

octane and n-dodecane) when the SP is less than 14.5 mm. A significant difference has recently been observed by Kang et al. [71] between the measured TSI values and linear prediction values. The measured TSI values for IPK and Jet A fuels was 13.3 and 20 respectively, whereas the linearly predicted values were 8.5 (IPK) and 13.4 (Jet A). Pepiot-Desjardins et al. [30] used the group contribution method for modeling the sooting tendency of oxygen containing fuel additives impact of oxygenated additives. In that study, every functional group was associated with a weight determined by the number of occurrences and then the TSI of the mixture was calculated from the mole fraction of the components.

The above-mentioned inconsistent results pertaining to the prediction of TSI using linear models shows the need of a reliable prediction method for TSI of surrogate fuels that can capture the non-linear, antagonistic and synergistic trends observed when blending multiple compounds [65]. It is evident that linear regression-based models like multiple linear regression (MLR) and partial least squares (PLS) are unable to reproduce the required intricacies of the problem. This calls for the use of machine learning (ML) based methods with non-linear decision boundaries. ANN is one of the techniques that fit this requirement. The goal of this study is to fit an ANN to the problem at hand: determining the TSI of a fuel given its chemical composition expressed as functional groups, molecular weight and BI (inputs). Figure 20 shows a general representation of the architecture of an ANN which is made up of an input layer, hidden layer and output layer. The ‘initial’ input layer is composed of the model inputs and the ‘outer’ layer, in the present scenario is comprised of a single node, representing the target (i.e. TSI). The nodes in the hidden layer(s) can be adjusted and is one of the various hyper-parameters that requires tuning. In

general, as the number of hidden nodes increase, the learning capacity of the network also increases and it becomes more flexible.

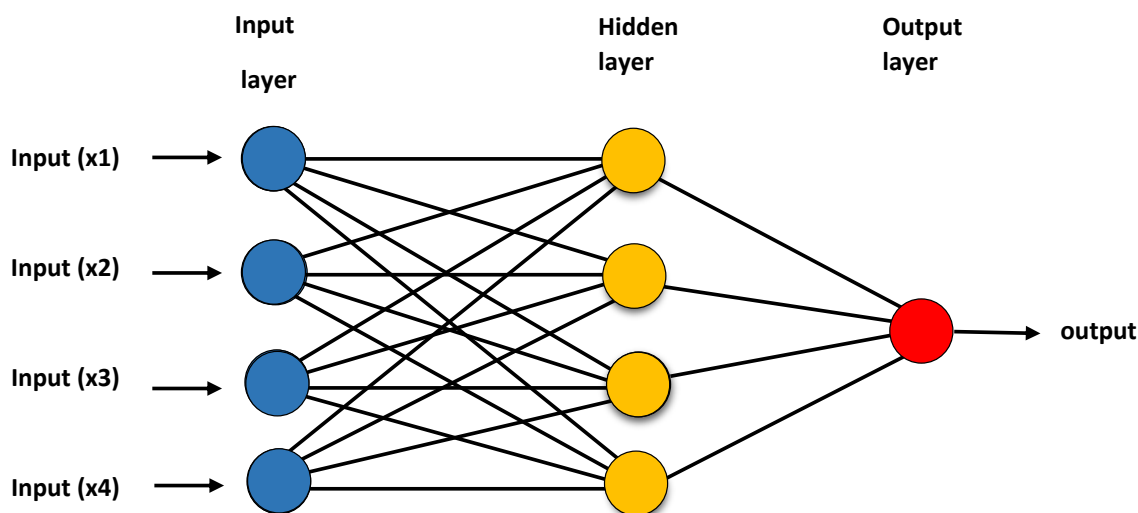


Fig. 18. A schematic representation of an ANN.

3.1 METHODOLOGY

3.1.1 Dataset

A dataset of 342 fuels comprising of 124 neat compounds (43 paraffins, 21 olefins, 15 naphthenes, 31 aromatics, 7 alcohols, and 7 ethers), 212 surrogate mixtures and 6 real fuels. The surrogate mixtures consist of the following compounds: n-heptane (hep), n-octane, iso-octane (2,2,4-trimethyl pentane), decalin, n-decane, n-dodecane, tetradecane, n-hexadecane (NHD), 2,2,4,4,6,8,8-heptamethylnonane (iso-cetane, HMN), cyclopentene, methylcyclohexane (MCH), benzene, toluene (tol), m-xylene, n-propyl benzene, naphthalene, 1,2,4 trimethylbenzene (1,2,4 TMB), 1,3,5-trimethylbenzene (1,3,5 TMB), tetralin, 1-methylnaphthalene (1-MN), 1-butanol (BuOH), hexanol, 1-undecanol (UnOH), tripropylene glycol methyl ether (TPGME). The real fuels used in the dataset are the fuels

for advanced combustion engines (FACE) gasoline's namely A, C, F, G, I and J. Other real fuels whose TSI data is available in the literature were not included in the dataset due to the non-availability of the ^1H nuclear magnetic resonance (NMR) data of those fuels. ^1H NMR spectra is needed for the estimation of the fuel functional groups of real fuels. The dataset was collected from the literature [15, 30, 33, 34, 45, 67-76, 78, 108-115] and the details (TSI values, mixture compositions) are provided in the Supplementary Material. The TSI data was used only from the sources which followed ASTM D1322 standard for measuring the SP. There are multiple TSI values reported for common fuels like n-heptane, 2,2,4-trimethylpentane, toluene etc. The differences in these values is mostly due to the difference of purity of the tested compounds and observer bias. For such cases, the average TSI values were used to overcome the uncertainty. Tables 1 and 2 below contain all the data, including the SP values for pure compounds and mixture compositions.

Table 4 : TSI of pure compounds

S.No	Name	TSI	Uncertainty	Reference
	Paraffins			
1.	Ethane	0		[1]
2.	propane	0.8	117%	[2]
3.	n-butane	1.4	14.29%	[2]
4.	isobutane	2.8		[2]
5.	n-pentane	1.5	15.38%	[2]
6.	isopentane	1.6	9%	[2]
7.	2,2-dimethylpropane	3.5	18.18%	[2]

8.	n-hexane	2.6	8%	[2]
9.	2-methylpentane	2.9	0%	[2]
10.	3-methylpentane	3	7.14%	[2]
11.	2,2-dimethylbutane	3.7	10.81%	[2]
12.	2,3-dimethylbutane	3.2	9%	[2]
13.	n-heptane	2.6	7.41%	[2]
14.	2-methylhexane	3.2	9%	[2]
15.	3-methylhexane	3.2	9%	[2]
16.	2,3-dimethylpentane	3.5	9%	[2]
17.	2,4-dimethylpentane	3.6	9%	[2]
18.	n-octane	3.2	0%	[2]
19.	2-methylheptane	3.5	9%	[2]
20.	3-methylheptane	3.7	9%	[2]
21.	4-methylheptane	4	9%	[2]
22.	3-ethylhexane	4	9%	[2]
23.	2,2-dimethylhexane	4.5	9%	[2]
24.	2,3-dimethylhexane	3.8	9%	[2]
25.	2,2,4-trimethylpentane(iso-octane)	6.4	10.71%	[2]
26.	2,3,3-trimethylpentane	5.7	9%	[2]
27.	2,3,4-trimethylpentane	5.7	9%	[2]
28.	2-methyle-3-ethylpentane	4.4	9%	[2]
29.	n-nonane	3.1	1-7%	[2]
30.	Isononane	3.8		[2]

31.	n-decane	4.2	1-7%	[2]
32.	n-undecane	4.5	1-7%	[2]
33.	n-dodecane	5.1	1-7%	[2]
34.	n-tridecane	5.2	9%	[2]
35.	n-tetradecane	5.4	9%	[2]
36.	Iso-cetane (2,2,4,4,6,8,8-heptamethylnonane)	23.6		[3]
37.	neopentane	3.5	1-7%	[4]
38.	2-methyloctane	3.8	1-7%	[4]
39.	4-methylhpetane	4	1-7%	[4]
40.	2,3 Dimethylhexane	3.8	1-7%	[4]
41.	2-methylpropane	2.2	9%	[5]
42.	2-methylbutane	1.6	9%	[5]
43.	Hexadecane	7.44		[6]
	Olefins			
44.	ethylene	0.7		[2]
45.	propylene	8.2	45.8%	[2]
46.	1,3-butadiene	35		[2]
47.	1-butene	6		[2]
48.	2-butene	5.9		[2]
49.	isobutene	6.6		[2]
50.	1-pentene	4.6	17%	[2]
51.	1-hexene	4.5	11.36%	[2]
52.	1-heptene	4.5	8.70%	[2]

53.	2-heptene	4.7	10.42%	[2]
54.	1-octene	5.8	1-7%	[2]
55.	trans 2-octene	4.4	9%	[2]
56.	1-nonene	7.4	1-7%	[2]
57.	1-decene	6.4	12.50%	[2]
58.	1-dodecene	8.4	1-7%	[2]
59.	1-tridecene	11	1-7%	[2]
60.	1-tetradecene	9.6	1-7%	[2]
61.	1-Hexadecene	11	1-7%	[2]
62.	1,5-cyclooctadiene	17	1-7%	[2]
63.	2,5-dimethyl-1,5-hexadiene	25		[2]
64.	2-methylpropene	4.8	9%	[5]
	Naphthenes			
65.	cyclopropane	5.4		[2]
66.	cyclopentene	16	6.06%	[2]
67.	cyclopentane	3.5		[2]
68.	methylcyclopentane	5	2.04%	[2]
69.	cyclohexane	3.5	1-7%	[2]
70.	cyclohexene	5.9	8.77%	[2]
71.	methylcyclohexane	4.9	1-7%	[2]
72.	1,3-dimethylcyclohexane	5.9		[2]
73.	cyclooctane	5.9	1-7%	[2]
74.	decahydronaphthalene (decalin)	15	1-7%	[2]

75.	bicyclohexyl	12	1-7%	[2]
76.	phenylcyclohexane	107.9	22.7	[7]
77.	cyclopropane	5.4		[2]
78.	ethylcyclohexane	5.4	1-7%	[2]
79.	4-methylcyclohexene	11	1-7%	[2]
	Aromatics			
80.	benzene	29	1.61%	[2]
81.	toluene	44	1-7%	[2]
82.	styrene	67	1-7%	[2]
83.	ethylbenzene	54	1-7%	[2]
84.	indene	62	1-7%	[2]
85.	1,3-dimethylbenzene(m-xylene)	42	1-7%	[2]
86.	1,4-dimethylbenzene(P-xylene)	42	1-7%	[2]
87.	1,2-dimethylbenzene(o-xylene or xylene)	49	15.69%	[2]
88.	1,2,3-trimethylbenzene(trimethylbenzenes)	52		[2]
89.	1,3,5-trimethylbenzene(milstone)	61	10%	[8]
90.	1,2,4-trimethylbenzene	61	10%	[8]
91.	propylbenzene	47	1-7%	[2]
92.	isopropylbenzene(cumene)	61	1-7%	[2]
93.	naphthalene	100	15.22	[2]
94.	1,2-dihydronaphthalene	87	10%	[8]
95.	tetralin	61	18%	[2]
96.	1,2-diethylbenzene(diethylbenzene)	60		[2]

97	1-isopropyl-4-methylbenzene (4-Isopropyltoluene or p-cymene)	61	36%	[2]
98	1,3-diethylbenzene(m-diethylbenzene)	60		[2]
99	n-butylbenzene	62	1-7%	[2]
100	1-methylnaphthalene	91	1-7%	[2]
101	(2,2-dimethylpropyl)-benzene(tert-pentylbenzene)(tert-amylbenzene)	58		[2]
102	(3-methylbutyl)-benzene(sec-pentylbenzene)(sec-amylbenzene)	58		[2]
103	n-pentylbenzene	50	1-7%	[2]
104	1,2-dimethylnaphthalene(dimethylnaphthalenes)	98		[2]
105	cyclohexylbenzene	78		[2]
106	1,3-diisopropylbenzene	51		[2]
107	s-butylbenzene	60		[2]
108	tert-butylbenzene	84		[2]
109	2-methylnaphthalene	89		[2]
110	1,2-dimethylnaphthalene (dimethylnaphthalene)	98		[2]
	Alcohols			
111	1-butanol	2.135	12.18%	[9]
112	1-pentanol	3.404	9.40%	[9]
113	2-pentanol	3.26	8.90%	[9]

114	1-hexanol	2.7	10.00%	[9]
115	3-methyl 1-butanol	4.38	7.76%	[9]
116	2-methyl 1-butanol(2-Methylbutan-1-ol)	5.12	7.03%	[9]
117	2-methyl 2-butanol	4.59	7.63%	[9]
	Ethers			
118	dimethoxymethane	4.13		[9]
119	methyl sec-butyl ether(sec butyle methyl ether)	3.49		[9]
120	methyl tert-butyl ether(methyl tert butyl ether)	5.46		[9]
121	1,2-dimethoxyethane	6.59		[9]
122	2-(2-methoxyethoxy)-ethanol(Diethylenglycol methylether)	3.34		[9]
123	ethyleneglycol monopropyl ether	6.29		[9]
124	2,2-dimethoxypropane(dimethoxypropane)	6.73		[9]
	Real fuels			
125	Face A gasoline	2.2	77.27%	[10]
126	Face C gasoline	4.4	27.27%	[10]
127	Face F gasoline	6.6	22.73%	[10]
128	Face G gasoline	22.1	61.09%	[10]
129	Face I gasoline	0.2	100.%	[10]
130	Face J gasoline	17.7	64.97%	[10]

Table 5: TSI of surrogate mixtures

S.No	Surrogate composition	TSI	Uncertainty	Ref.
246.	3-methylpentane/Tetralin (94/6 mol%)	4.3		[10]
247.	3-methylpentane/Indane (80/20 mol%)	16.8		[10]
248.	3-methylpentane/Tetralin (70/30 mol%)	25.2		[10]
249.	3-methylpentane/Tetralin (68/32 mol%)	23.8		[10]
250.	n-heptane/Toluene (53/47 mol%)	15.3		[10]
251.	60% iso-octane/40% toluene (vol%)	24	10%	[11]
252.	75% iso-octane/25% toluene (vol%)	17	10%	[11]
253.	80% iso-octane/20% toluene (vol%)	16	10%	[11]
254.	85% iso-octane/15% toluene (vol%)	13.5	10%	[11]
255.	90% iso-octane/10% toluene (vol%)	10.7	10%	[11]
256.	95% iso-octane/5% toluene (vol%)	9.7	10%	[11]
257.	11% iso-cetane/ 89% 1,2,4 TMB (vol%)	61	10%	[11]
258.	24% iso-cetane/ 76% 1,2,4 TMB(vol%)	53	10%	[11]
259.	42% iso-cetane/ 58% 1,2,4 TMB (vol%)	52	10%	[11]
260.	53% iso-cetane/ 47% 1,2,4 TMB (vol%)	46	10%	[11]
261.	66% iso-cetane/ 34% 1,2,4 TMB (vol%)	37	10%	[11]
262.	81% iso-cetane/ 19% 1,2,4 TMB (vol%)	30	10%	[11]
263.	10%iso-octane /90%toluene (vol%)	41	10%	[11]

264.	24%iso-octane /76%toluene (vol%)	34	10%	[11]
265.	39%iso-octane /61%toluene (vol%)	29	10%	[11]
266.	49%iso-octane /51%toluene (vol%)	24	10%	[11]
267.	66%iso-octane /34%toluene (vol%)	17	10%	[11]
268.	72%iso-octane /28%toluene (vol%)	15	10%	[11]
269.	78%iso-octane /22%toluene (vol%)	13	10%	[11]
270.	85%iso-octane /15%toluene (vol%)	11	10%	[11]
271.	92%iso-octane /8%toluene (vol%)	8.3	10%	[11]
272.	17% m-xylene /83 %n-dodecane (vol%)	13	10%	[11]
273.	33% m-xylene /67 %n-dodecane (vol%)	18	10%	[11]
274.	34% m-xylene /66 %n-dodecane (vol%)	18	10%	[11]
275.	36% m-xylene /64 %n-dodecane (vol%)	20	10%	[11]
276.	37% m-xylene /63 %n-dodecane (vol%)	20	10%	[11]
277.	39% m-xylene /61 %n-dodecane (vol%)	21	10%	[11]
278.	50% m-xylene /50 %n-dodecane (vol%)	24	10%	[11]
279.	65% m-xylene /35 %n-dodecane (vol%)	32	10%	[11]
280.	78% m-xylene /22 %n-dodecane (vol%)	36	10%	[11]
281.	88% m-xylene /12 %n-dodecane (vol%)	43	10%	[11]
282.	75%1,2,4 TMB /25%1-MN (vol%)	69	10%	[11]

283.	60%1,2,4 TMB /40%1-MN (vol%)	80	10%	[11]
284.	40%1,2,4 TMB /60%1-MN (vol%)	83	10%	[11]
285.	25%1,2,4 TMB /75%1-MN (vol%)	85	10%	[11]
286.	95%decalin /5%1-MN (vol%)	23	10%	[11]
287.	89%decalin /11%1-MN (vol%)	28	10%	[11]
288.	78%decalin /22%1-MN (vol%)	38	10%	[11]
289.	68%decalin /32%1-MN (vol%)	46	10%	[11]
290.	52%decalin /48%1-MN (vol%)	57	10%	[11]
291.	32%decalin /68%1-MN (vol%)	75	10%	[11]
292.	13%decalin /87%1-MN (vol%)	89	10%	[11]
293.	98%MCH /2%1-MN (vol%)	8.7	10%	[11]
294.	95%MCH /5%1-MN (vol%)	12	10%	[11]
295.	91%MCH /9%1-MN (vol%)	17	10%	[11]
296.	81%MCH /19%1-MN (vol%)	25	10%	[11]
297.	72%MCH /28%1-MN (vol%)	34	10%	[11]
298.	62%MCH /38%1-MN (vol%)	40	10%	[11]
299.	42%MCH /58%1-MN (vol%)	64	10%	[11]
300.	21%MCH /79%1-MN (vol%)	81	10%	[11]
301.	50% n-heptane,50% tol (mol %)	26.5		[7]

302.	66% n-heptane,34% tol (mol %)	18.1		[7]
303.	75% n-heptane,25% tol (mol %)	14.3		[7]
304.	50% isooctane,50% tol (mol %)	37.7		[7]
305.	60% isooctane,40% tol (mol %)	29.4		[7]
306.	66% isooctane,33% tol (mol %)	27.6		[7]
307.	75% isooctane,25% tol (mol %)	17.9		[7]
308.	80% isooctane,20% tol (mol %)	16.1		[7]
309.	90% isooctane,10% tol (mol %)	10.5		[7]
310.	95% isooctane,5% tol (mol %)	6.7		[7]
311.	JP-8 (38.2% n-dodecane /37.2% iso-octane /24.6% propylbenzene) mole%	18.3		[12]
312.	Sasol IPK(16% n-dodecane /64.7% iso-octane /19.3% propylbenzene) mole%	15.7		[12]
313.	Shell SPK (74.6% n-decane /4.5% n-dodecane /12.2% iso-octane /8.7% propylbenzene) mole%	9.1		[12]
314.	HRJ CamelL (61.1% n-dodecane /29.2% iso-octane /9.6% propylbenzene) mole%	11.4		[12]
315.	HRJ Tallow (59.5% n-dodecane /31.5% iso-octane /9% propylbenzene) mole%	11		[12]
316.	Hep 90%, Tol 10% (vol%)	2.1		[13]
317.	Hep 70%, Tol 30% (vol %)	11		[13]

318.	Hep 50%, Tol 50% (vol%)	19.9		[13]
319.	Hep 30%, Tol 70% (vol%)	30.5		[13]
320.	45% n-dodecane and 55% m-xylene (vol%)	28.15		[14]
321.	73% n-dodecane and 27% Alpha-methylnaphthalene (vol%)	29		[14]
322.	naphthalene 15/BB 85 (vol%)	26.4		[15]
323.	naphthalene 10/BB 90 (vol%)	21.68		[15]
324.	naphthalene 5/BB 95 (vol%)	18.05		[15]
325.	tetralin 40/BB 60 (vol%)	31.1		[15]
326.	tetralin 20/BB 80 (vol%)	21.73		[15]
327.	tetralin 10/BB 90 (vol%)	18.23		[15]
328.	cyclopentene 60/BB 40 (vol%)	15.7		[15]
329.	cyclopentene 40/BB 40 (vol%)	15.42		[15]
330.	cyclopentene 20/BB 40 (vol%)	15.22		[15]
331.	n-octane 10/BB 90 (vol%)	13.16		[15]
332.	n-octane 20/BB 80 (vol%)	12.7		[15]
333.	n-octane 40/BB 60 (vol%)	10.88		[15]
334.	n-octane 60/BB 40 (vol%)	9.07		[15]
335.	86% Decalin/14% Isooctane (vol%)	16.3		[16]
336.	21% Toluene/79% Isooctane (vol%)	12.9		[16]

337.	8% Tetralin/92% Isooctane(vol%)	12.9		[16]
338.	5% Methylnaphthalene/95% Isooctane (vol%)	15		[16]
339.	48.73% n-decane /27.76% iso-octane/23.51% toluene (vol%)	18.55		[17]
340.	41.73% n-dodecane /35.43% iso-octane/22.84% toluene (vol%)	19.19		[17]
341.	52.47% % n-decane/18.33% iso-octane/2.20%n propylbenzene/27% 1,3,5-trimethylbenzene (vol%)	21.47		[17]
342.	42.45% n-dodecane /29.10%% iso-octane/14.57%n-propylbenzene/13.88% 1,3,5-trimethylbenzene (vol%)	21.47		[17]
343.	40% toluene/60% iso-octane(vol%)	22.56		[18]
344.	20% toluene/80% iso-octane(vol%)	15.32		[18]
345.	10% toluene/90% iso-octane(vol%)	12.85		[18]
346.	5% toluene/95% iso-octane (vol%)	10.15		[18]
347.	35% toluene/65% n-heptane (vol%)	15.58		[18]
348.	10% benzene /90%BB (vol%)	16.78		[18]
349.	20% benzene /80%BB (vol%)	18.16		[18]
350.	40% benzene /60%BB (vol%)	22.84		[18]
351.	15%1-methylnaphtalene /85% BB (vol%)	26.47		[18]
352.	10%1-methylnaphtalene /90% BB (vol%)	24.69		[18]
353.	5%1-methylnaphtalene /95% BB (vol%)	19		[18]

354.	10% toluene/90% n-heptane (vol%)	8.12		[18]
355.	20% toluene/80% n-heptane (vol%)	9.87		[18]
356.	40% toluene/60% n-heptane (vol%)	17.67		[18]
357.	50/50 iC8/iC16 (mol %)	15.2	3.29%	[3]
358.	Jet-A surrogate volume % (47.06% n-dodecane +16.69% iso-cetane +24.19% decalin+12.06% Toluene)	13.4		[19]
359.	IPK surrogate volume % (14.16% n-dodecane +31.41% iso-cetane +40.16% isooctane+14.27 decalin)	8.5		[19]
360.	40.41% n-dodecane, 29.48% iso-octane, 7.28% 1,3,5-trimethylbenzene, 22.83% n-propylbenzene (mol%)	20.3	10%	[20]
361.	NHD(n-hexadecane) 85%(V) + 15% (V) TMB(1,2,4 trimethylbenzene)	21.9		[21]
362.	NHD(n-hexadecane) 8%(V) + 2% (V) TMB (1,2,4 trimethylbenzene)	27		[21]
363.	NHD (n-hexadecane) 75%(V) + 15% (V) TMB (1,2,4 trimethylbenzene)	35.2		[21]
364.	NHD (n-hexadecane)7%(V) + 3% (V) TMB (1,2,4 trimethylbenzene)	41.3		[21]
365.	NHD (n-hexadecane)65%(V) + 35% (V) TMB (1,2,4 trimethylbenzene)	45		[21]
366.	NHD (n-hexadecane)6%(V) + 4% (V) TMB (1,2,4 trimethylbenzene)	47.8		[21]

367.	NHD (n-hexadecane)5%(V) + 5% (V) TMB (1,2,4 trimethylbenzene)	54.3		[21]
368.	TPGME(tri(propylene glycol)methyl ether) 80% + TMB 20% (1,2,4 trimethylbenzene)	19.8		[21]
369.	TPGME(tri(propylene glycol)methyl ether)75% + TMB 25% (1,2,4 trimethylbenzene)	30.4		[21]
370.	TPGME(tri(propylene glycol)methyl ether) 70% + TMB 30% (1,2,4 trimethylbenzene)	37.9		[21]
371.	TPGME(tri(propylene glycol)methyl ether) 65% + TMB 35% (1,2,4 trimethylbenzene)	44.2		[21]
372.	TPGME(tri(propylene glycol)methyl ether)60% + TMB 40% (1,2,4 trimethylbenzene)	52.8		[21]
373.	TPGME(tri(propylene glycol)methyl ether) 50% + TMB 50% (1,2,4 trimethylbenzene)	63.6		[21]
374.	TPGME(tri(propylene glycol)methyl ether)20% + TMB 80% (1,2,4 trimethylbenzene)	73.4		[21]
375.	TPGME(tri(propylene glycol)methyl ether)70% + 1,2,4 trimethylbenzene) 30%	37.5		[21]
376.	TPGME(tri(propylene glycol)methyl ether)50% +NHD(n-hexadecane)20%(V)+ TMB (1,2,4 trimethylbenzene) 30%	37.5		[21]
377.	TPGME(tri(propylene glycol)methyl ether)23% +NHD(n-hexadecane)47%(V)+ TMB (1,2,4 trimethylbenzene) 30%	37.8		[21]

378.	TPGME(tri(propylene glycol)methyl ether)11% +NHD(n-hexadecane)59%(V)+ TMB (1,2,4 trimethylbenzene) 30%	37.9		[21]
379.	TPGME(tri(propylene glycol)methyl ether)50% +TMB (1,2,4 trimethylbenzene) 50%	59.1		[21]
380.	TPGME(tri(propylene glycol)methyl ether)23.5% +NHD(n-hexadecane)26.5%(V)+ TMB (1,2,4 trimethylbenzene) 50%	57.4		[21]
381.	TPGME(tri(propylene glycol)methyl ether)11.5% +NHD(n-hexadecane)38.5%(V)+ TMB (1,2,4 trimethylbenzene) 50%	56.3		[21]
382.	NHD(n-hexadecane)50%(V)+ TMB (1,2,4 trimethylbenzene) 50%	56.3		[21]
383.	BuOH(1-butanol)70% + TMB (1,2,4 trimethylbenzene) 30%	13.2		[21]
384.	BuOH(1-butanol)38% +NHD(n-hexadecane)32%(V)+ TMB (1,2,4 trimethylbenzene) 30%	19.6		[21]
385.	BuOH(1-butanol)18.5% +NHD(n-hexadecane)51.5%(V)+ TMB (1,2,4 trimethylbenzene) 30%	26.1		[21]
386.	HMN(2,2,4,4,6,8,8-heptamethylnonane)70% +TMB (1,2,4 trimethylbenzene) 30%	55.2		[21]
387.	HMN(2,2,4,4,6,8,8-heptamethylnonane)35% +NHD(n-hexadecane)35%(V)+ TMB (1,2,4 trimethylbenzene) 30%	47.6		[21]
388.	UnOH(1-undecanol)70% + TMB (1,2,4 trimethylbenzene) 30%	28.6		[21]
389.	UnOH(1-undecanol)43.5% +NHD(n-hexadecane)26.5%(V)+ TMB (1,2,4 trimethylbenzene) 30%	32		[21]

390.	0%(V) n-dodecane, 35%(V)n-tetradecane,0%(V) isooctane,35% (V)decalin, and 30 %(V) 1,3,5-trimethylbenzene	28.76	14.1	[22]
391.	0%(V) n-dodecane, 80%(V)n-tetradecane, 0%(V) isooctane, 5% (V)decalin, and 15 %(V) 1,3,5-trimethylbenzene	16.00	15.8	[22]
392.	80%(V) n-dodecane, 0%(V)n-tetradecane,10%(V) isooctane,0% (V)decalin, and 10 %(V) 1,3,5-trimethylbenzene	11.29	18.2	[22]
393.	0%(V) n-dodecane, 80%(V)n-tetradecane,5%(V) isooctane,0% (V)decalin, and 15 %(V) 1,3,5-trimethylbenzene	15.05	16.1	[22]
394.	0%(V) n-dodecane, 0%(V)n-tetradecane,0%(V) isooctane,90% (V)decalin, and 10 %(V) 1,3,5-trimethylbenzene	23.16	14.6	[22]
395.	70%(V) n-dodecane, 0%(V)n-tetradecane,0%(V) isooctane,0% (V)decalin, and 30 %(V) 1,3,5-trimethylbenzene	25.15	14.4	[22]
396.	40%(V) n-dodecane, 40%(V)n-tetradecane,10%(V) isooctane,0% (V)decalin, and 10 %(V) 1,3,5-trimethylbenzene	11.14	18.2	[22]
397.	47.9%(V) n-dodecane, 12.9%(V)n-tetradecane,7.5%(V) isooctane,7.5% (V)decalin, and24.2 %(V) 1,3,5-trimethylbenzene	21.00	14.8	[22]

398.	52.9%(V) n-dodecane, 12.9%(V)n-tetradecane,12.5%(V) isooctane,7.5% (V)decalin, and 14.2 %(V) 1,3,5-trimethylbenzene	15.09	16.2	[22]
399.	12.9%(V) n-dodecane, 52.9%(V)n-tetradecane,7.5%(V) isooctane,12.5% (V)decalin, and 14.2 %(V) 1,3,5-trimethylbenzene	18.09	15.3	[22]
400.	0%(V) n-dodecane, 80%(V)n-tetradecane,0%(V) isooctane,0% (V)decalin, and 20 %(V) 1,3,5-trimethylbenzene	20.60	14.8	[22]
401.	35%(V) n-dodecane, 0%(V)n-tetradecane,35%(V) isooctane,0% (V)decalin, and 30 %(V) 1,3,5-trimethylbenzene	25.06	14.5	[22]
402.	52.9%(V) n-dodecane, 12.9%(V)n-tetradecane7.5%(V) isooctane,7.5% (V)decalin, and 19.2 %(V) 1,3,5-trimethylbenzene	18.44	15.2	[22]
403.	35%(V) n-dodecane, 0%(V)n-tetradecane,0%(V) isooctane,35% (V)decalin, and 30 %(V) 1,3,5-trimethylbenzene	26.38	14.4	[22]
404.	80%(V) n-dodecane, 0%(V)n-tetradecane,5%(V) isooctane,0% (V)decalin, and 15 %(V) 1,3,5-trimethylbenzene	15.02	16.2	[22]
405.	0%(V) n-dodecane, 0%(V)n-tetradecane,90%(V) isooctane,0% (V)decalin, and 10 %(V) 1,3,5-trimethylbenzene	12.51	17.4	[22]

406.	12.9%(V) n-dodecane, 12.9%(V)n-tetradecane,7.5%(V) isooctane,42.5% (V)decalin, and 24.2 %(V) 1,3,5-trimethylbenzene	26.91	14.3	[22]
407.	25.8%(V) n-dodecane, 25.8%(V)n-tetradecane,15%(V) isooctane,15% (V)decalin, and 18.3 %(V) 1,3,5-trimethylbenzene	20.62	14.8	[22]
408.	12.9%(V) n-dodecane, 12.9%(V)n-tetradecane,7.5%(V) isooctane,52.5% (V)decalin, and 14.2 %(V) 1,3,5-trimethylbenzene	21.64	14.7	[22]
409.	0%(V) n-dodecane, 75%(V)n-tetradecane,0%(V) isooctane,0% (V)decalin, and 25 %(V) 1,3,5-trimethylbenzene	21.62	14.6	[22]
410.	80%(V) n-dodecane, 0%(V)n-tetradecane,0%(V) isooctane,5% (V)decalin, and 15 %(V) 1,3,5-trimethylbenzene	14.60	16.3	[22]
411.	0%(V) n-dodecane, 0%(V)n-tetradecane,35%(V) isooctane,35% (V)decalin, and 30 %(V) 1,3,5-trimethylbenzene	29.88	14.4	[22]
412.	0%(V) n-dodecane, 0%(V)n-tetradecane,0%(V) isooctane,70% (V)decalin, and 30 %(V) 1,3,5-trimethylbenzene	32.36	14.2	[22]
413.	0%(V) n-dodecane, 80%(V)n-tetradecane,5%(V) isooctane,5% (V)decalin, and 10 %(V) 1,3,5-trimethylbenzene	12.23	17.5	[22]

414.	0%(V) n-dodecane, 80%(V)n-tetradecane,10%(V) isooctane,0% (V)decalin, and 10 %(V) 1,3,5-trimethylbenzene	12.72	17.2	[22]
415.	40%(V) n-dodecane, 40%(V)n-tetradecane,0%(V) isooctane,0% (V)decalin, and 20 %(V) 1,3,5-trimethylbenzene	18.15	15.3	[22]
416.	0%(V) n-dodecane, 70%(V)n-tetradecane,0%(V) isooctane,0% (V)decalin, and 30 %(V) 1,3,5-trimethylbenzene	26.74	14.2	[22]
417.	0%(V) n-dodecane, 40%(V)n-tetradecane,50%(V) isooctane,0% (V)decalin, and 10 %(V) 1,3,5-trimethylbenzene	12.27	17.5	[22]
418.	0%(V) n-dodecane, 0%(V)n-tetradecane,70%(V) isooctane,0% (V)decalin, and 30 %(V) 1,3,5-trimethylbenzene	25.11	14.7	[22]
419.	0%(V) n-dodecane, 0%(V)n-tetradecane,0%(V) isooctane,80% (V)decalin, and 20 %(V) 1,3,5-trimethylbenzene	27.40	14.3	[22]
420.	12.9%(V) n-dodecane, 52.9%(V)n-tetradecane,12.5%(V) isooctane,7.5% (V)decalin, and 14.2 %(V) 1,3,5-trimethylbenzene	16.34	15.7	[22]
421.	12.9%(V) n-dodecane, 52.9%(V)n-tetradecane,7.5%(V) isooctane,7.5% (V)decalin, and 19.2 %(V) 1,3,5-trimethylbenzene	18.42	15.2	[22]

422.	0%(V) n-dodecane, 35%(V)n-tetradecane,35%(V) isooctane,00% (V)decalin, and 30 %(V) 1,3,5-trimethylbenzene	26.26	14.4	[22]
423.	80%(V) n-dodecane, 0%(V)n-tetradecane,5%(V) isooctane,5% (V)decalin, and 10 %(V) 1,3,5-trimethylbenzene	10.91	18.4	[22]
424.	52.9%(V) n-dodecane, 12.9%(V)n-tetradecane,7.5%(V) isooctane,12.5% (V)decalin, and 14.2 %(V) 1,3,5-trimethylbenzene	16.32	15.8	[22]
425.	80%(V) n-dodecane, 0%(V)n-tetradecane,0%(V) isooctane,10% (V)decalin, and 10 %(V) 1,3,5-trimethylbenzene	12.47	17.4	[22]
426.	0%(V) n-dodecane, 40%(V)n-tetradecane,0%(V) isooctane,50% (V)decalin, and 10 %(V) 1,3,5-trimethylbenzene	18.99	15.1	[22]
427.	0%(V) n-dodecane, 80.0%(V)n-tetradecane,0%(V) isooctane, 10.0% (V)decalin, and 10.0 %(V) 1,3,5-trimethylbenzene	13.13	17.0	[22]
428.	0%(V) n-dodecane, 0%(V)n-tetradecane,45.0%(V) isooctane,45.0% (V)decalin, and 10.0 %(V) 1,3,5-trimethylbenzene	18.28	15.4	[22]
429.	40.0%(V) n-dodecane, 40.0%(V)n-tetradecane,0%(V) isooctane,10.0% (V)decalin, and 10.0 %(V) 1,3,5-trimethylbenzene	11.98	17.7	[22]

430.	12.9%(V) n-dodecane, 47.9%(V)n-tetradecane,75.%(V) isooctane,0% (V)decalin, and 10.0 %(V) 1,3,5-trimethylbenzene	19.78	15.0	[22]
431.	40.0%(V) n-dodecane, 0%(V)n-tetradecane,50.0%(V) isooctane,0% (V)decalin, and 10.0 %(V) 1,3,5-trimethylbenzene	11.20	18.2	[22]
432.	0%(V) n-dodecane, 0%(V)n-tetradecane,80.0%(V) isooctane,0% (V)decalin, and 20.0 %(V) 1,3,5-trimethylbenzene	19.93	15.2	[22]
433.	80.0%(V) n-dodecane, 0%(V)n-tetradecane,0%(V) isooctane,0% (V)decalin, and 20.0 %(V) 1,3,5-trimethylbenzene	18.19	15.3	[22]
434.	40.0%(V) n-dodecane,0%(V)n-tetradecane,0%(V) isooctane, 50.0% (V)decalin, and 10.0 %(V) 1,3,5-trimethylbenzene	18.22	15.3	[22]
435.	35.0%(V) n-dodecane, 35.0 %(V)n-tetradecane,0%(V) isooctane,0 % (V)decalin, and 30.0%(V) 1,3,5-trimethylbenzene	25.98	13.8	[22]
436.	75.0%(V) n-dodecane, 0%(V)n-tetradecane,0%(V) isooctane,0 % (V)decalin, and 25.0 %(V) 1,3,5-trimethylbenzene	19.30	15.1	[22]
437.	12.9%(V) n-dodecane, 12.9%(V)n-tetradecane,52.5%(V) isooctane,7.5% (V)decalin, and 14.2%(V) 1,3,5-trimethylbenzene	16.18	15.9	[22]

438.	12.9%(V) n-dodecane, 12.9%(V)n-tetradecane,42.5%(V) isooctane,7.5% (V)decalin, and 24.2 %(V) 1,3,5-trimethylbenzene	22.47	14.7	[22]
439.	52% iso-cetane 23% n-dodecane 25% 1,3,5-trimethylbenzene (vol%)	29	10%	[8]
440.	64% iso-cetane 23% n-dodecane 13% methylnaphthalene (vol%)	29.3	10%	[8]
441.	54% iso-octane 18% n-dodecane 28% 1,3,5-trimethylbenzene (vol%)	24	10%	[8]
442.	57.38% heptane 42.61 %toluene (mol%)	13.61	4.15%	[23]
443.	42.95% heptane 31.90 %toluene 25.14% hexanol (mol%)	10.86	4.15%	[23]
444.	79.6%n-decane 20.4% Toluene (mol%)	11.53	15%	[24]
445.	59.2% n-decane 40.8% Toluene (mol%)	18.58	15%	[24]
446.	19.6% n-decane 80.4% Toluene (mol%)	32.25	15%	[24]
447.	39.8% n-decane 60.2% Toluene (mol%)	25.28	15%	[24]
448.	80.7% n-decane 19.3 % iso-octane (mol%)	4.83	15%	[24]
449.	60.3% n-decane 39.7% iso-octane (mol%)	5.17	15%	[24]
450.	40% n-decane 60% iso-octane (mol%)	5.52	15%	[24]
451.	20.1% n-decane 79.9% iso-octane (mol%)	5.86	15%	[24]
452.	26.1% n-decane+ 26% iso-octane+ 47.9 toluene (mol%)	21.46	15%	[24]
453.	34.9% n-decane+ 35.4% iso-octane+ 29.8% toluene (mol%)	15.37	15%	[24]

454.	17.2% n-decane+ 67.8% iso-octane+ 15% toluene (mol%)	10.83	15%	[24]
455.	17.7% n-decane+ 43.9% iso-octane+ 38.4% toluene (mol%)	18.5	15%	[24]
456.	68.3% n-decane+ 17.2% iso-octane+ 14.5% toluene (mol%)	9.79	15%	[24]
457.	37.6% n-decane+ 45.4% iso-octane+ 17% toluene (mol%)	11.15	15%	[24]

3.1.2 Computing the functional groups

The functional groups of the neat compounds were calculated from their molecular structure. Two compounds are taken here as examples for explaining the methodology of calculating the functional groups. n-heptane, which has a molecular weight (MW) of 100 g/mol consists of two paraffinic CH₃ and five paraffinic CH₂ groups. The MW of the CH₃ groups is 15 g/mol and that of the CH₂ groups is 14 g/mol. There is a total of two CH₃ groups and five CH₂ groups present in n-heptane that makes the total weight contribution of paraffinic CH₃ groups and paraffinic CH₂ groups as 30% and 70% respectively. Using a similar analogy, 1-heptene can be divided into four paraffinic CH₂, one paraffinic CH₃ and two olefinic –CH=CH₂ groups. Thus, their contributions expressed in terms of weights % in 1-heptene are 57.1%, 15.3% and 29.6 %, respectively. The functional group distribution for a few pure compounds is shown in Fig. 21. Expressing the functional groups in terms of weight percentage (wt%) was preferred over mole percentage (mol%) to avoid over/under representation which was seen when mol% was

used as shown in previous study [79].

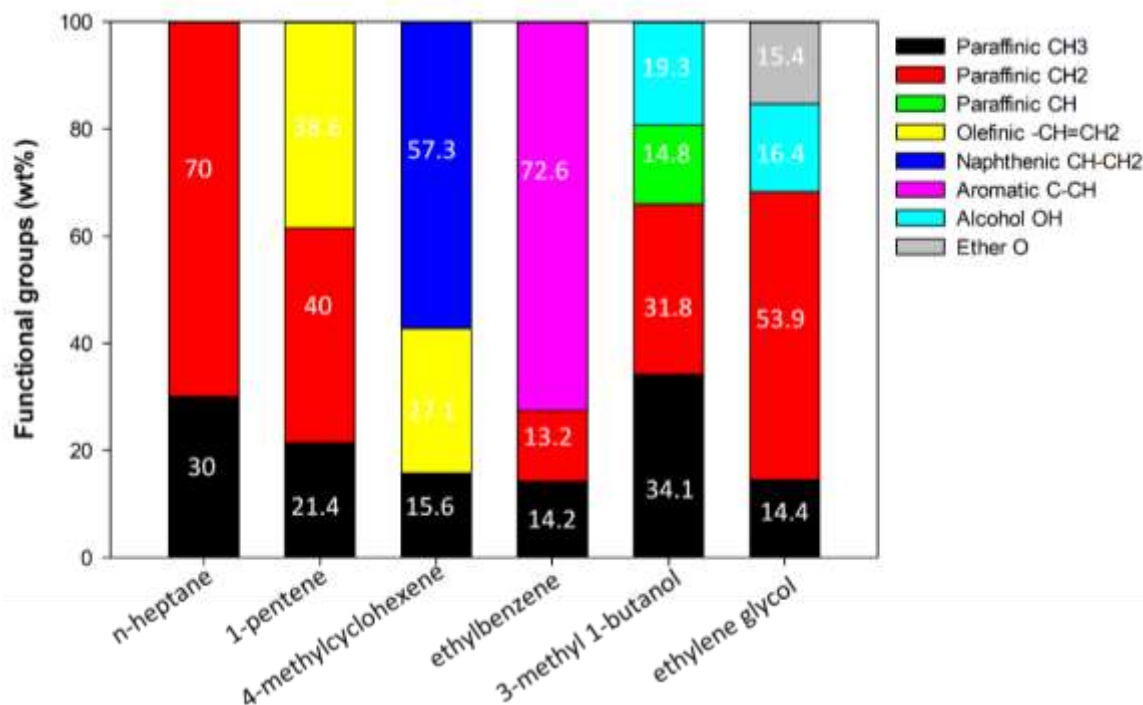


Fig. 19. Functional groups distribution of some pure compounds

Fuel surrogates are usually expressed and blended in volume fractions. The functional group distribution of surrogate mixtures was calculated by using the densities of the pure compounds and blend ratio. A functional group calculator (excel file) containing several compounds has been added in the GitHub repository (link provided at the end) which can be used by the readers to convert blends into their constituent functional groups. Fig. 22 shows the functional groups of some surrogate mixtures reported in the literature. The total summation of the functional groups of some of the mixtures does not equal 100% because quaternary paraffinic carbons were not considered in the present work as input criteria. The present functional group approach for property prediction was developed primarily for predicting properties of real petroleum fuels by evaluating the functional

groups using ^1H NMR spectroscopy which is fast and quantitative. As quaternary paraffinic carbons are not bonded to an H atom, it becomes very difficult to calculate the quantity of quaternary paraffinic carbons present in the sample using ^1H NMR. Therefore, these were ignored. Also, from detailed hydrocarbon analysis of a number of standard gasolines it has been observed that the quantity of quaternary paraffinic carbons in petroleum fuels is very less ($< 2\%$) [9]. The contribution of quaternary aromatic carbons, however, is considered in the present approach as these are substantial and cannot be ignored. The methodology and formulae for including the quaternary aromatic carbons from ^1H NMR is presented in our previous work [47]. Also, the quantity of quaternary paraffinic carbons present in neat compounds in our dataset is also very low, where more than 90 percent of functional groups sum to 100. The formulae for calculating the functional groups of real fuels from ^1H NMR spectra in a tabulated form is reported in our previous work [42].

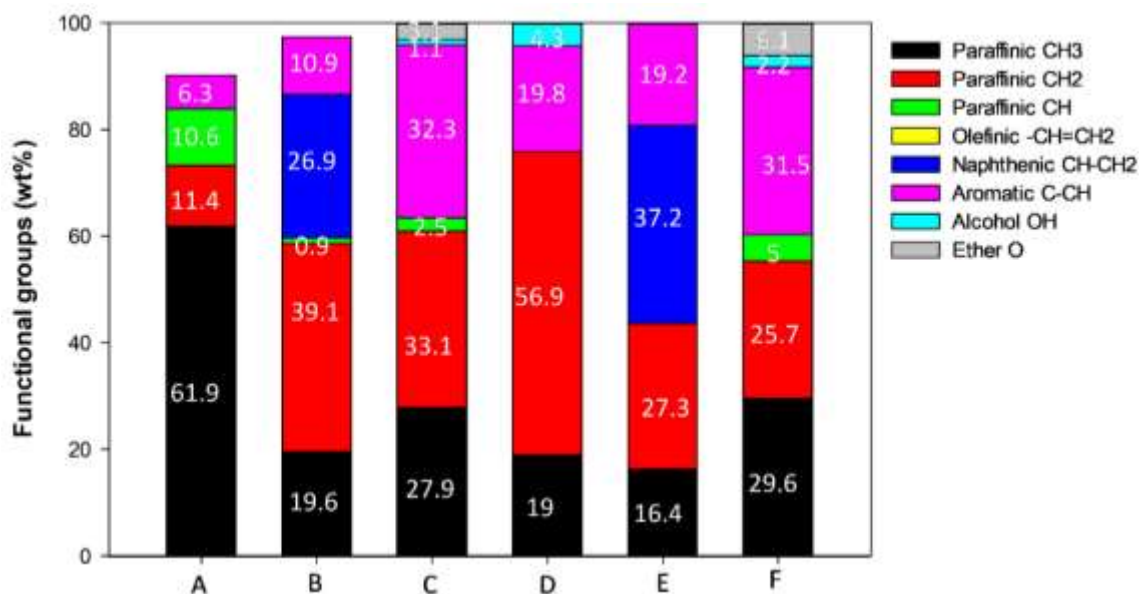


Fig. 20. Functional group distribution of some fuel surrogate mixtures. The compositions in vol% are expressed as follows: (A) 5% methylnaphthalene + 95% iso-octane, (B) Jet-A (47.06% n-dodecane + 16.69% iso-cetane + 24.19% decalin + 12.06%

tol), (C) 11.5% TPGME + 38.5% NHD + 50% 1,2,4 TMB, (D) 43.5% UnOH + 26.5% NHD + 30% 1,2,4TMB, (E) 35% n-tetradecane + 35% decalin + 30% 1,3,5 TMB, (F) 23.5% TPGME + 26.5% NHD + 50% 1,2,4 TMB .

Molecular weight (MW) has a considerable impact on the physical properties of a fuel, and therefore it has been included as an input feature. The average molecular weight (AMW) of the surrogate mixtures were calculated from the blend compositions, and the AMW of the 6 real fuel were obtained from [15]. Another input parameter namely the BI was coined by Abdul Jameel et al. [79] and it quantifies the branching of a molecule by including the effect of position and size of the methyl/methylene branches. BI is calculated as the ratio of the number of carbon atoms connected to the longest chain in the molecule divided by the carbon atoms present in the longest chain. A position index (PI) term is also calculated for each carbon atom connected to the longest chain and this PI term is added in the numerator. For example, 2-methylpentane has 1 carbon (in the form of the methyl branch) connected to the longest chain which has 5 carbon atoms. Since the methyl branch in position 2 is in the outermost position it is assigned a PI of 0. The BI of 2-methylpentane is calculated as $\{(1+0)/5 = 0.2\}$. The methyl branch in 3-methylpentane is one position away from the outermost position and is assigned a PI of 0.5. Its BI is calculated as $\{(1+0.5)/5 = 0.3\}$. By using BI as an input feature, we are now able to distinguish 2-methylpentane and 3-methylpentane, which have similar functional groups but different properties. The BI of aromatic molecules is also calculated after redrawing the structure in the form of an i-paraffin. The BI of surrogate mixtures is calculated from the sum of the product of component BI and corresponding molar fractions. BI of real fuels was calculated from the ^1H NMR spectra of the fuel. Providing a complete theoretical background of BI

definition and rationale is out of scope of the present work and the readers are directed here [79].

3.1.3 ANN development

The dataset was split into training and test sets comprising of 70% and 15% of the data, respectively. The remaining 15% data was used as validation set which was used to tune the hyper-parameters. A feedforward ANN optimized through backpropagation was developed. The final evaluation is based on the model's performance on the test set, which was never used to steer the ANN, thus reducing potential test set biases. The model optimization was carried out using neural network tool in Matlab. The validation set has been exclusively used for assessing the models through fine controlling and the test set was only used at the end. The hyper-parameters tuned on the validation set include: the number of hidden neurons per layer and the number of hidden layers. After running a large number of iterations (epochs), a local minimum was found for a certain ANN. The parameters of the code were optimized (i.e., the parameters that generate minimal errors) for getting the best models. Once the optimal topology has been determined, the ANN was retrained and validated and then finally tested on the test set.

In this work, the datasets include 342 points where each point has 10 input features and one output, TSI. The Pearson correlation, which correlates between TSI and each feature, is shown below in Fig. 23. Pearson correlation is a most commonly used correlation in regression techniques to ascertain the linear relationship between two variables. In the present case, the Pearson correlation shows the effectiveness (or correlation) of the input features with each other and on the output (TSI). This effectiveness is represented by the numbers found in the cells of intersection between the rows and

columns. For example, the two values of 0.88 and 0.83 (in red color) represent a very strong correlation between BI and TSI, and between aromatic C-CH groups and TSI, respectively. On the other hand, the ether O groups represented by the number of 0.0094 indicates a very weak correlation between ethers and TSI. The aromatic C-CH groups and BI have the most significant impact on TSI whereas the ether O groups appear to impart the least effect numerically. However, when the features behave non-linearly, combinations of seemingly insignificant input features may produce significant results.

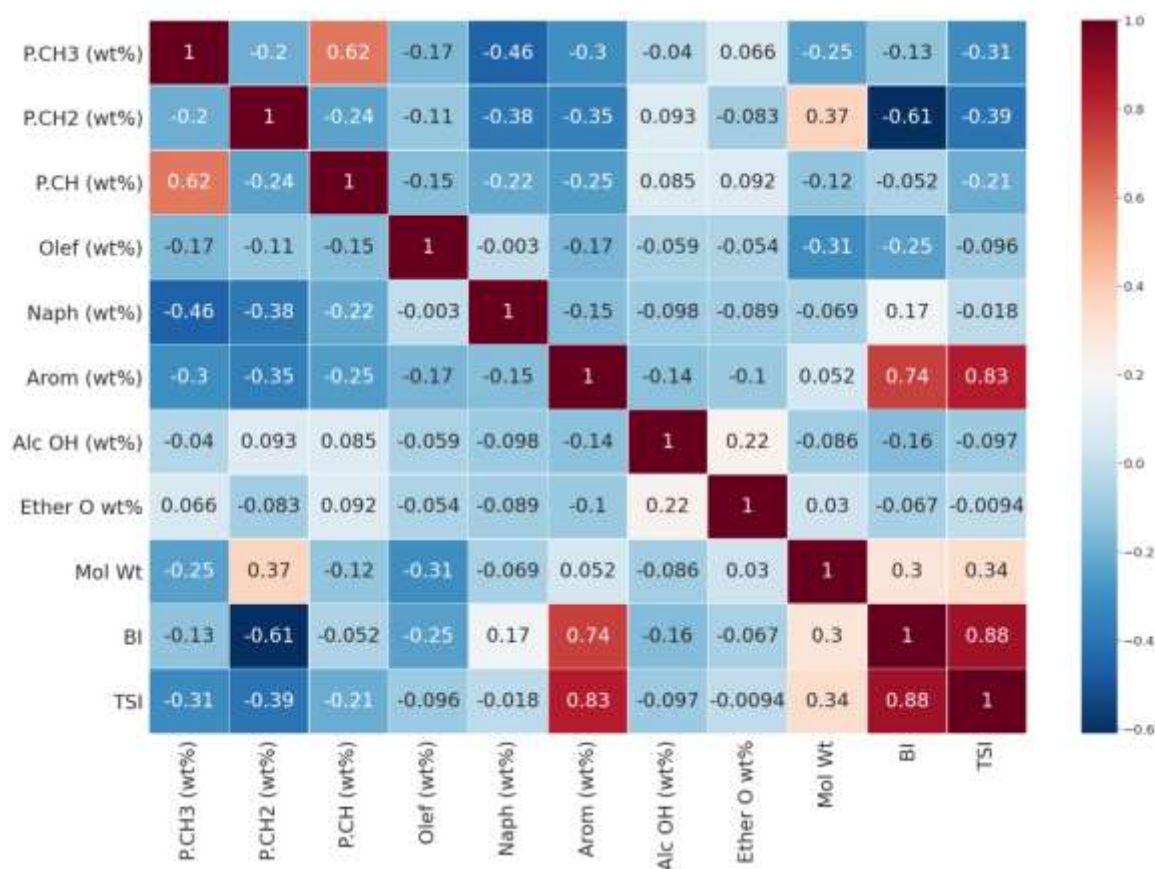


Fig. 21. The inputs and the output features represented by Pearson correlation.

The search space for all these parameters, depicted in Table 2, is very large, and determining each in separate levels reduces computational costs significantly. That being

said, only varying a single parameter is likely to lead to suboptimal choices and thus some variance in the other parameters is maintained in order to account for their interdependence. For example, when targeting the number of hidden layers, the results are an average over a subset of the tested number of hidden neurons, and epochs. Once a parameter has been determined, it is fixed for the subsequent levels until all parameters are finalized.

Table 6: Range of hyper-parameters employed

Parameter	Range
Number of hidden layers	$[1 \leq x \leq 3]$
Number of neurons	$[10 \leq x \leq 20]$
Epochs	$[1 \leq x \leq 10]$
Loss function	Mean squared error (MSE)

3.2 Results & Discussions

The TSI of a compound/mixture depend on its molecular structure and in the following section, the individual effect of the ten input parameters on TSI will be discussed.

3.2.1 Paraffinic CH₃ groups

In general, paraffins have lower sooting tendencies compared to other hydrocarbon classes like olefins, naphthenes and aromatics having the same carbon number. n-Hexane has a lower TSI of 2.6 compared to 1-hexene, cyclohexane and benzene which have 4.5, 3.5 and 29 as TSI, respectively. Figure 24 shows the effect of paraffinic CH₃ groups on the TSI of pure compounds and surrogate fuels, respectively. Ethane which

is exclusively composed of paraffinic CH_3 groups has the lowest TSI of 0 (as measured by a diffusion flame [45]) in the dataset. The TSI of i-paraffins, increases with increase in the paraffinic CH_3 content. Eight carbon i-paraffins namely 2-methylheptane, 2,2-dimethylhexane and 2,2,4-trimethylpentane possess 3, 4 and 5 paraffinic CH_3 groups respectively. The TSI values of these compounds are 3.5, 4.5 and 6.4 respectively, which shows an increase in TSI with increase in the methyl content for i-paraffins. This trend is also observed in other i-paraffinic molecules having the same carbon number. The paraffinic CH_3 group tends to increase the TSI of aromatic hydrocarbons due to the presence of the three hydrogen atoms, which can form a stabilized benzyl group due to H abstraction. This is often followed by ring additions that results in the formation of polyaromatic hydrocarbons (PAH) species. Paraffinic CH_3 groups connected to an aromatic ring possesses the ability to cause a growth of sp^2 carbons with a hexagonal network [129]. Also, addition of paraffinic CH_3 groups to aromatic rings reduces the concentrations of paraffins and oxygenates in the soot formed [88].

Paraffinic CH_3 groups could possibly be the most abundant group in gasolines and their surrogates as indicated [15] and play a major role in the ignition of surrogate mixtures [62]. Figure 5b shows the impact of paraffinic CH_3 groups on the surrogate mixtures present in the dataset. In the binary mixtures comprising ‘decalin-1-MN’, ‘NHD-1,2,4 TMB’, ‘TPGME-1,2,4 TMB’, ‘m-xylene-n-dodecane’ and ‘n-decane-iso-octane’, the TSI increases with the paraffinic CH_3 groups and an opposing trends is observed in the remaining blends due to pronounced effects of other molecular groups. For example, there is a rapid reduction in TSI of 1-MN due to the addition of MCH even though the change in the paraffinic CH_3 groups of the resulting mixture is minor. This is apparently due to the

reduction of aromatic groups, which strongly influences the TSI more than the paraffinic CH_3 groups. Error bars were added to those datapoints where the uncertainty associated with the measurements was presented in the original source.

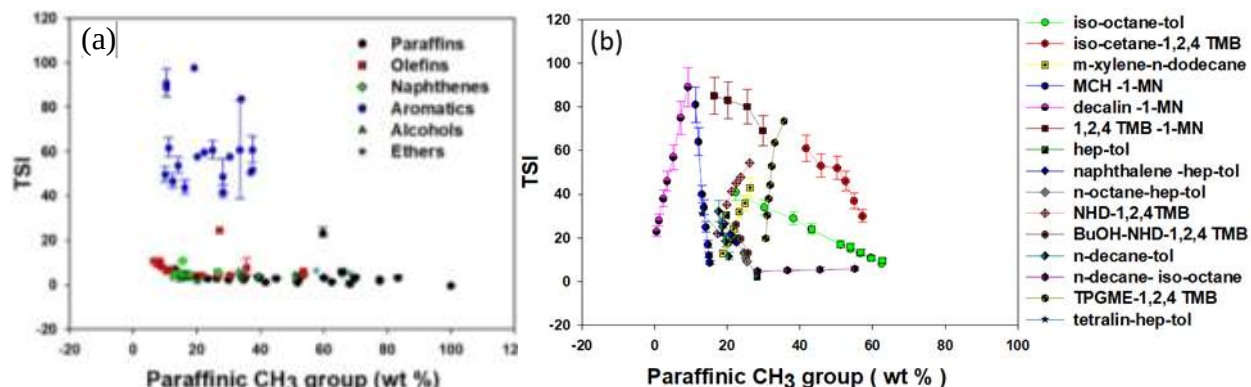


Fig. 22. Effect of paraffinic CH_3 groups on TSI of (a) pure compounds; and (b) surrogate fuel mixtures

3.2.2 Paraffinic CH_2 groups.

The quantity the paraffinic groups (CH_2 and CH_3) has a significant impact on the combustion behavior of paraffins [80] and it has been experimentally observed that paraffinic fuel mixtures with similar CH_2/CH_3 ratios result in similar ignition delays [62]. A larger proportion of paraffinic CH_2 groups in branched paraffins indicates a high degree of linearity which, as branched paraffins have higher sooting propensities when compared to their straight chain counterparts [83]. The impact of paraffinic CH_2 groups on the TSI of pure compounds and the surrogate mixtures is presented in Fig. 25. The TSI of n-paraffins increases with increase in carbon number and this shows that paraffinic CH_2 groups correlate positively with TSI, but this however could also be due to the increase in molecular size which has also been shown to increase sooting propensity [84]. When the

size of the paraffinic side chains connected to the aromatic rings is increased, the sooting propensity has also been shown to increase. This is because the hydrocarbon radicals formed due to the decomposition of the chain react with benzylic groups [85]. This is followed by the formation of naphthalene and other polyaromatics, which act as soot precursors. The sooting propensities of primary, secondary and tertiary alkylaromatics show large variations due to the differences associated with the soot formation and growth pathways [85]. From the Fig. 6b it is observed that as the paraffinic CH₂ groups increase the TSI decreases for all the surrogate mixtures except ‘n-decane-iso-octane’ where there is a very minor reduction.

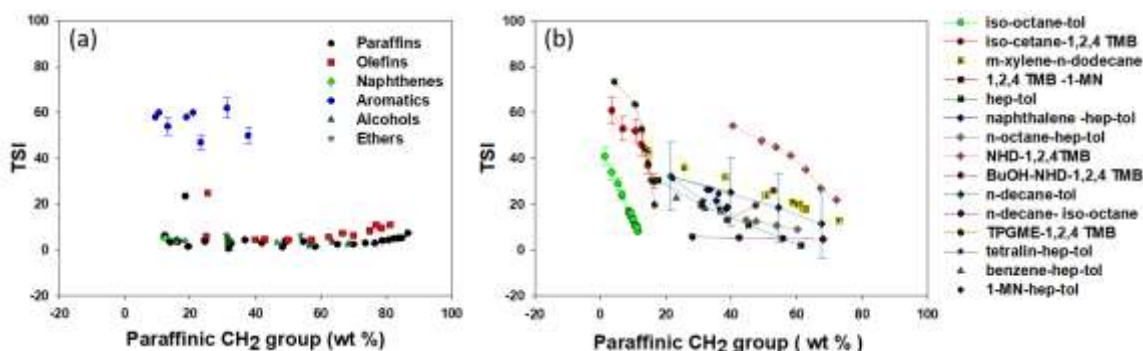


Fig. 23. Effect of paraffinic CH₂ groups on TSI of (a) pure compounds; and (b) surrogate fuel mixtures

3.2.3 Paraffinic CH groups

The TSI of i-paraffins tends to increase with increase in the paraffinic CH group. 2-methylpentane which has 1 CH group has a lower TSI of 2.9 compared to 2,3-dimethylbutane which has a TSI of 3.2. Similarly, 2-methylhexane possesses a lower TSI of 3.2 when compared with 2,4-dimethylpentane which has a higher TSI of 3.6 owing to the two CH groups. This is generally true for i-paraffins having the same carbon number.

The impact of paraffinic CH groups on TSI is presented in Fig. 26. Interestingly it can be seen that the TSI of the blends ‘iso-octane-tol’, ‘isocetane-1,2,4 TMB’ and ‘TPGME-1,2,4 TMB’ is found to reduce with an increase in the paraffinic CH content. The reason for this is that in all these blends the net aromatic content of the mixture reduces when the paraffinic CH content is increased. It can now be inferred that aromatics produce a marked effect on the TSI of the blends when compared with the effect of the paraffinic CH groups. This behavior has also been observed for ignition delay measurements in blends of ‘hep-iso-octane-tol’ and ‘iso-octane-tol’ where the effect of paraffinic CH groups is masked by the aromatics groups [79].

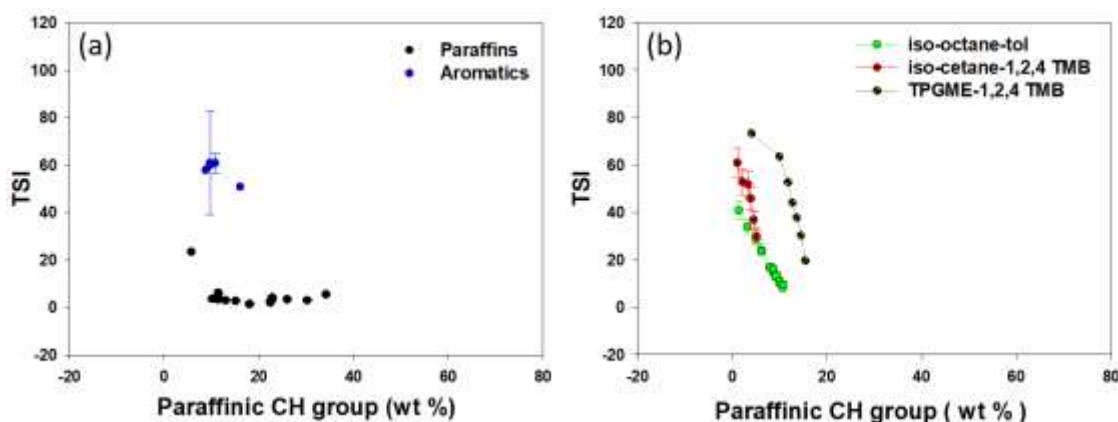


Fig. 24. Effect of paraffinic CH groups on TSI of (a) pure compounds; and (b) surrogate fuel mixtures

3.2.4 Olefinic -CH=CH₂ groups

The quantity of olefinic groups present in gasoline and diesel is usually low when compared to other hydrocarbon groups and have a large impact on the oxidative stability and autoignition behavior. Olefins generally have a higher tendency to soot compared to

their n-paraffin/i-paraffin counterparts. For example, 1-pentene and 1-octene have higher TSI's of 4.6 and 5.8 respectively, when compared with n-pentane (TSI, 1.5) and n-octane (TSI, 3.2). Figure 27 shows the impact of the olefinic $-\text{CH}=\text{CH}_2$ groups on the TSI of the pure compounds. It is noteworthy to say that olefinic double bond in cyclic fuels like cyclopentene and cyclohexene promotes soot formation and it has been experimentally shown that these unsaturated olefinic groups have a more significant impact on sooting propensity when compared to methyl substitution [81].

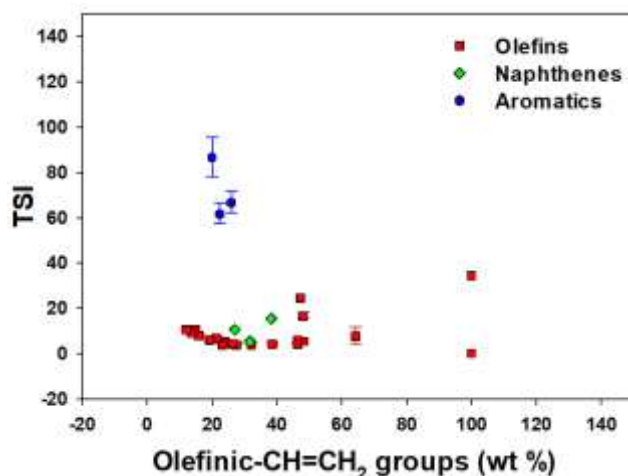


Fig. 25. Effect of olefinic $-\text{CH}=\text{CH}_2$ groups on TSI of pure compounds

3.2.5 Naphthenic $-\text{CH}-\text{CH}_2$ groups

Generally, naphthenes exhibit higher tendencies for soot formation when compared with paraffins and olefins of similar size. Addition of naphthenes to a coflow diffusion flame of n-heptane has shown an increase in the yellow luminosity of the flame along its midline, and hence indicating that naphthenes possess a higher sooting propensity than paraffins [81]. This is due to the formation of benzene and poly-aromatic rings that acts as soot precursors. The number and size of the soot particles measured at low flame heights also increased significantly due to doping of the cyclic fuels with n-heptane [81].

Figure 28 shows the impact of the naphthenic $-\text{CH}-\text{CH}_2$ groups on the TSI of pure compounds and surrogate mixtures. The TSI increases with increase in naphthenic groups for ‘tetralin-hep-tol’. But for the blends ‘MCH-1-MN’ and ‘decalin-1-MN’ the TSI decreases with increases in naphthenic groups because the aromatic content reduces with MCH addition. This shows that aromatics have a more pronounced impact on TSI than naphthenes.

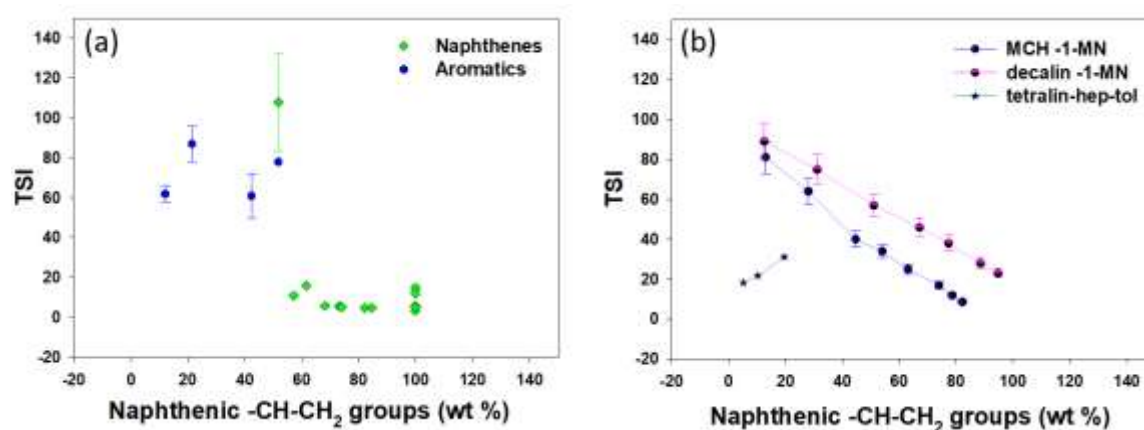


Fig. 26. Effect of naphthenic $-\text{CH}-\text{CH}_2$ groups (wt %) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures

3.2.6 Aromatic C-CH groups

Aromatics form a significant part of gasoline, diesel and jet fuels and their presence in these fuels varies depending on the parent crude, refining practices and target application. Aromatic compounds like benzene, toluene, xylenes, alkylbenzenes, naphthalene are found significantly in petroleum fuels [86]. Aromatics have been known to be significant contributors to soot formation and a number of studies have discussed their impact [85, 87-89]. Aromatic fuels produce flames with a high concentration of PAH species observed even at lower flame heights and an increase of soot precursors due to dehydrogenation and subsequent ring formation/addition is observed in the post oxidation

zone [90]. It has been reported that soot formed from aromatic fuels produce graphitized structures [130] and the soot particles are more complex morphologically and structurally when compared with aliphatic fuels [89]. Aromatic fuels produce soot that has a high degree of carbonization due to the high temperatures associated with aromatic flames. Soot obtained from toluene diffusion flames showed denser and significantly larger particles when compared with the soot collected from n-heptane flames [88]. Differences in soot size and morphology sampled from engines and flames (for both aromatic and aliphatic fuels) show a much larger variation due to the different local conditions of temperature and pressure [131]. One of the reasons why aromatics are more notorious for soot formation is because they may possibly remain intact during combustion, thus creating a pathway for growth of soot precursors [132]. Figure 29 shows change in TSI of pure compounds and surrogate mixtures with changes in the aromatic content. It can be observed that there is a unanimous increase in the TSI of the surrogate mixtures with increasing aromatic content.

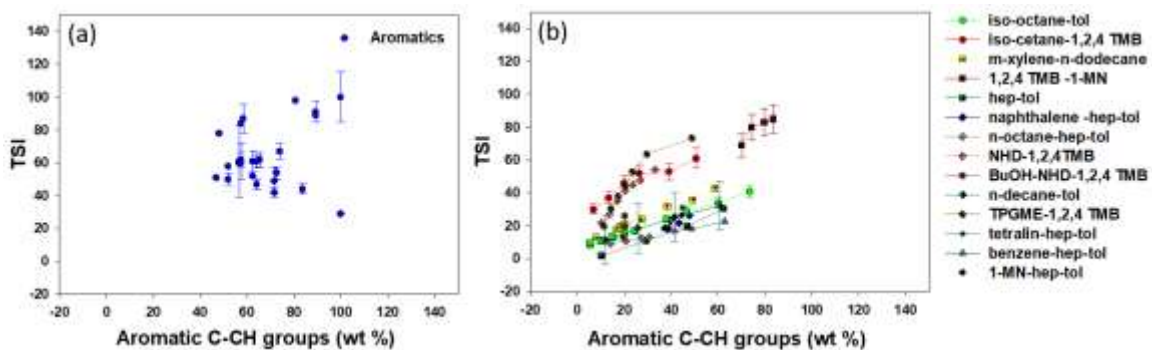


Fig. 27. Effect of Aromatic C-CH groups (wt %) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures

3.2.7 Alcoholic OH groups

The addition of alcohols to petroleum fuels lowers the reactivity of the fuel and also reduces the low temperature heat release (LTHR) as the OH group acts as a radical

scavenger [91]. Alcohols increase the combustion efficiency of hydrocarbon fuels and alcohols like ethanol are routinely blended with gasoline to act as an octane booster. It has been shown that ethanol OH groups have a more pronounced effect on gasoline octane number than any other hydrocarbon functional groups [16]. In general, primary alcohols possess lower TSI than n-paraffins and olefins of similar carbon numbers. For instance, TSIs of 1-hexanol and 1-hexene are 2.7 and 4.5, respectively. n-Butanol possesses the lowest TSI of 2.1 compared to other alcoholic compounds in this dataset because of its high OH content at 23 wt%. Secondary alcohols have been shown to possess higher sooting propensities compared to both primary alcohols and n-paraffins of the same carbon number. This is primarily due to the four center reactions (e.g. water elimination reaction seen in 2-butanol) which proceed at quicker rates in secondary alcohols compared to primary alcohols [133]. The impact of alcoholic OH groups on pure compounds and surrogate mixtures is shown in Fig. 30. In the mixtures, it can be observed that as the wt% of the alcoholic OH groups increase, the TSI of the mixtures decreases. Interestingly an opposing trend is observed in one of the two data series corresponding to the 'TPGME-NHD-1,2,4-TMB' blend. Although the wt% of the OH groups is similar in both the series, the ratio of aromatic to OH groups is consistently greater in the series where the opposing trend of increasing TSI is observed. This again shows that aromatic groups have a more dominating effect on TSI as discussed earlier.

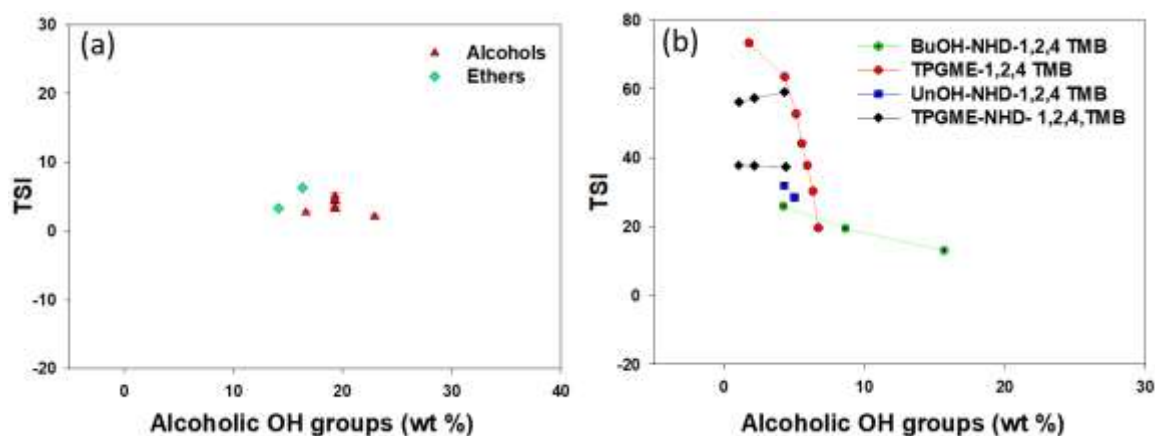


Fig. 28. Effect of alcoholic OH groups (wt %) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures

3.2.8 Ether O groups

Several studies [92-94] reported in the literature have treated the oxidation reaction of ethers with rules similar to that of paraffins. For a fixed carbon number, ether molecules possess the lowest sooting tendencies compared to both alcohol and hydrocarbon molecules. The oxygen atom in an ether molecule breaks the continuity of the carbon chain and as a result the reaction products are smaller hydrocarbon species that are likely to oxidize and less prone to form PAH soot precursors. A number of ether compounds like dimethoxymethane, diethylether, polyoxymethylene dimethyl ethers (PODE) etc. have been used as diesel additives for reducing soot emissions. A recent study [95] on a premixed laminar flame of dimethylether showed that there was no soot formation even under rich conditions. This is because of the lack of C-C bonds in dimethylether. When dimethylether was mixed with acetylene, which is notorious as a soot precursor, the mixture produced very little soot at an equivalence ratio of 1. The soot formation was found to increase when the equivalence ratio was increased to 2, but the volume of soot formed was found to decrease when the ratio of dimethylether in the blend was increased. The

effect of ether O groups on the TSI of pure compounds and surrogate mixtures is presented in Fig. 31. For blends of ‘TPGME-1,2,4 TMB’ the TSI reduces significantly as the ether groups increase, whereas for ‘TPGME-NHD-1,2,4 TMB’ the TSI increases slightly due to increase in aromatic groups.

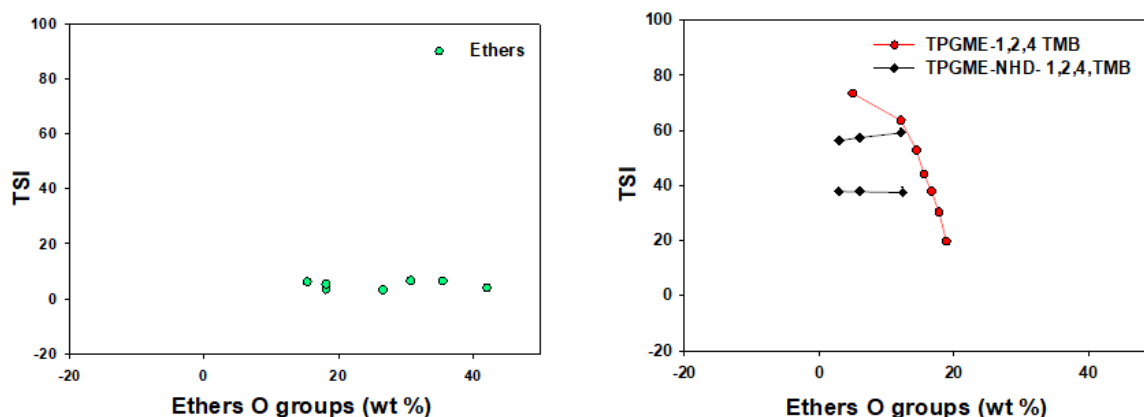


Fig. 29. Effect of ethers O groups (wt %) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures

3.2.9 Molecular weight

The sooting propensity of compounds generally increases with increase in the MW and this trend is observed for all the chemical classes in the dataset. Experimental soot measurements performed using a diesel engine fueled with blends of n-decane and n-hexadecane showed that the amount of soot formed increased with an increase in the MW of the fuel mixture [96]. Similarly experiments performed using a jet flame and a gas turbine fueled with ‘n-heptane and n-dodecane’ and ‘n-dodecane and n-hexadecane’ blends showed that the soot volume fractions recorded increased with increase in MW of the fuel mixture for both premixed and non-premixed flames [84]. Figure 32 shows the impact of molecular weight on TSI of pure compounds and surrogate mixtures. The TSI of n-paraffins steadily increases with increases in carbon number, whereas the TSI of i-

paraffins increases with carbon number provided the degree of branching is held constant. This trend is also seen in olefins, naphthenes, aromatics, alcohols and ethers. For the surrogate mixtures, there is an increase in TSI with molecular weight for ‘MCH-1-MN’, ‘decalin-1-MN’ and ‘BuOH-NHD-1,2,4 TMB’. For all other surrogate blends, an increase in molecular weight is followed by a reduction in aromatic content and as a result, the TSI decreases.

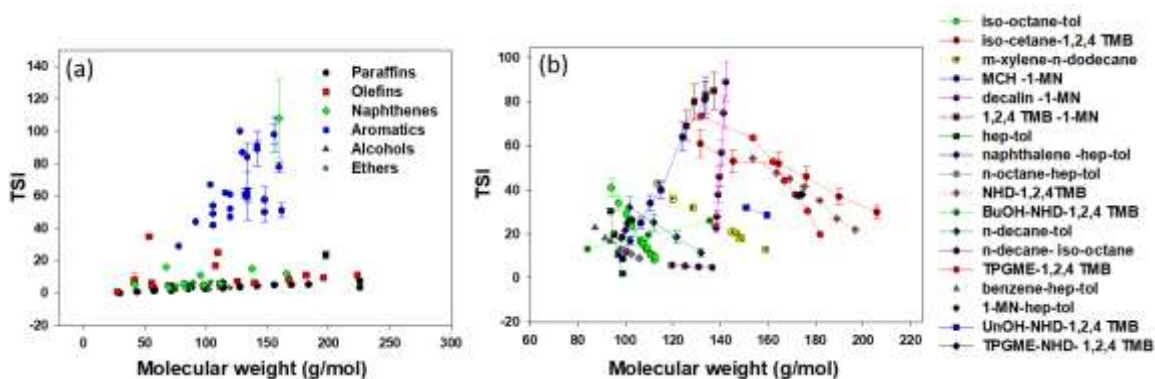


Fig. 30. Effect of Molecular weight (g/mol) on TSI of (a) pure compounds; and
(b) surrogate fuel mixtures

3.2.10 Branching index (BI)

Several works have shown that the sooting propensity of neat compounds increases with increase in its degree of branching provided the carbon number remains the same. Additionally, the position of the branching on the carbon chain also has a significant impact on the physical, chemical and combustion behavior of the compounds. For example, 2-methylheptane (TSI, 3.5), 3-methylheptane (TSI, 3.7) and 4-methylheptane (TSI, 4) have the same carbon number and functional group distribution but their TSI's vary on account of the position of the branching on the carbon chain. To consider the effect of branching by including the position of the branches, Abdul Jameel et al. [79] defined the BI which

can numerically capture the effect of branching by including the position effect. BI can be calculated not only for paraffins but also for ringed structures with side chains. Providing the definition and explanation of the BI is out of scope of the present work, which can be obtained from here [79]. The BI of 2-methylheptane, 3-methylheptane and 4-methylheptane is 0.14, 0.21 and 0.28 respectively, and this can now explain the differences in their TSI discussed earlier. Figure 33 shows the effect of BI on pure compounds and surrogate mixtures, and it can be observed that an increase in the BI results in an increase in the TSI. This trend can be spotted in both the pure compounds and all the reported surrogate

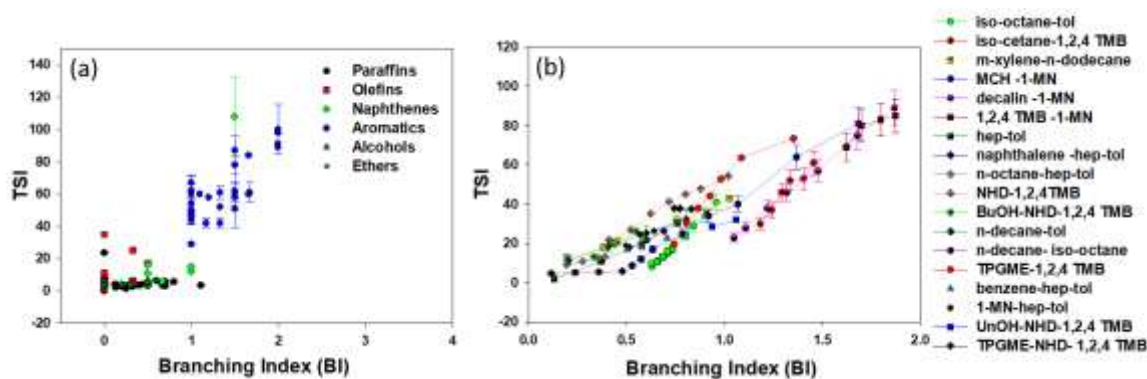


Figure 31.. Effect of branching index (BI) on TSI of (a) pure compounds; and (b) surrogate fuel mixtures

3.2.11 Final ANN Model

The ANN model was developed by following the above-mentioned methodology for predicting the TSI from the described input features and has been added in the supplementary material. The finalized hyper-parameters determined by optimizing the structure of the ANN model are presented in Table 3. The final architecture of the model is depicted in Fig. 34.

Table 7: The optimized hyper-parameters of the ANN model

Parameter	Description
Hidden layers numbers	1
Units' numbers (neurons)	10
Epochs	256
Learning rate	0.0265

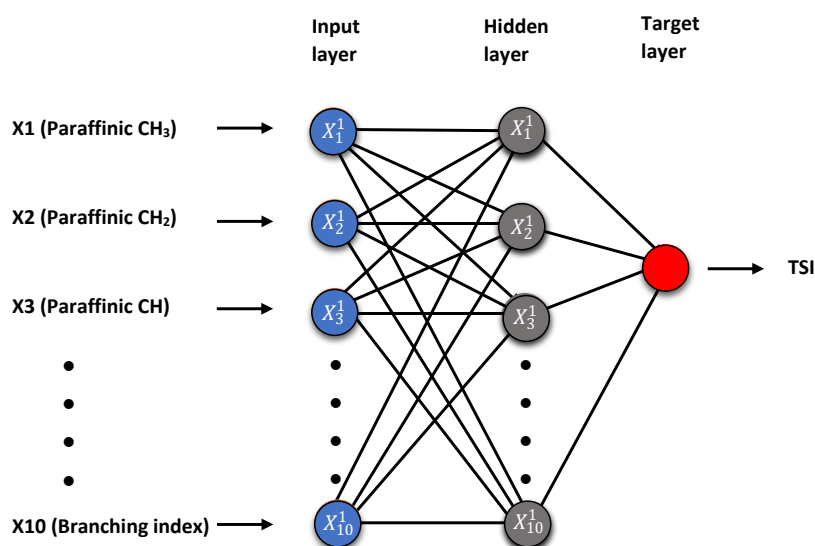


Fig. 32. Architecture of the ANN model developed for TSI prediction.

The model performance was analyzed by calculating the average of the TSI predictions by applying the model on the test set. It is important to indicate that the test set comprising 15% of the data was only used for final model testing and was never used to train or fine-tune the model. As stated before, the test set was automatically chosen and

based on our inspection contained 39% pure components and 61% surrogate mixtures. The performance of the final model can be observed by comparing the measured TSI values against the predicted values in the test set and the plot is shown in Fig. 35. The regression coefficient (R^2) obtained for the fit is 0.97. As a comparison we tested the methodology of Yan et al.[32] to predict the TSI of the entries in the present test set and obtained an R^2 value of 0.86. The reason of low correlation coefficient in [64] could be due to the difficulty in reproducing the non-linear behavior which can be captured by advanced techniques like ANN. One important indicator of the uniqueness of our approach is that no two fuels that have the same TSI, have the same input features in the dataset containing 342 fuels.

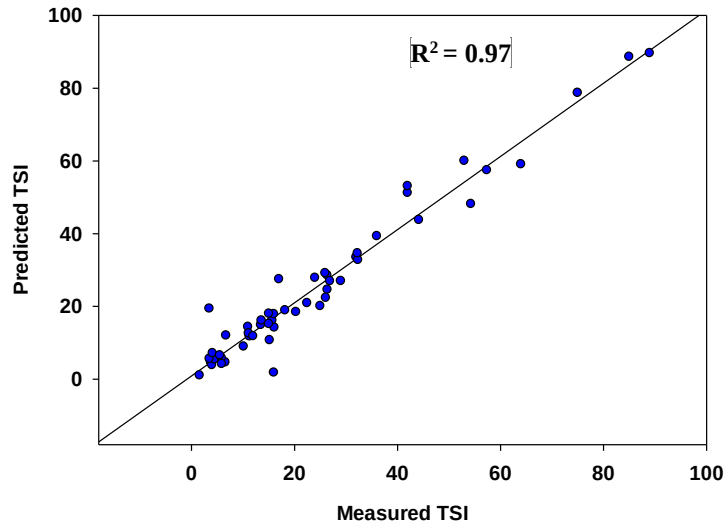


Fig. 33. Comparison between predicted and measured TSI values

In Fig. 36, the absolute differences between the predicted and measured TSI shows a complete view of the errors and outliers. There are a few big errors that

considerably raise the error metrics of the final model. The ANN may struggle in accurately predicting the TSI for those fuels that are statistically different compared to those in the dataset that do not fit the suggested trend or have unique PAH formation pathways like cyclohexene that follow a unique retro-Diels-Alder mechanism [134]. The average of the absolute and percentage errors obtained in the present study are 2.46 and 2.39%, respectively. These numbers are promising when compared against the uncertainty associated with experimental measurement of TSI. The average error of prediction when the model is applied against the entire dataset (training, validation and test set) was found to be lower at 2.01 which shows that the ANN model is well trained and is likely to perform well when tested against new molecules/blends.

The present model can also be applied for predicting the TSI of real petroleum fuels provided their functional groups could be calculated using techniques like nuclear magnetic resonance (NMR) spectroscopy, which is ideally suited for the purpose. The methodology to calculate the hydrocarbon functional groups and BI for petroleum fuels using ^1H NMR spectroscopy is reported in our previous work [79]. Oxygenates like alcohols and ethers are usually blended externally to hydrocarbon fuels in known quantities and therefore the alcoholic OH and ether O groups can be evaluated from the molecular structure of the compounds added. The final model has been added to the GitHub repository (<https://github.com/mohammed-Qasem/A-prediction-model-of-TSI>) for use by the readers.



Fig. 34. Absolute error between the measured and the predicted TSI values.

3.3 Conclusion

A dataset of 342 fuels consisting of 43 paraffins, 21 olefins, 15 naphthenes, 31 aromatics, 7 alcohols, 7 ethers, 212 surrogate mixtures and 6 gasoline's was utilized to develop a machine learning based model using ANN that can be applied for predicting the TSI of neat compounds, surrogate mixtures and real fuels composed of the above said chemical classes. The Pearson correlation indicated that the aromatic groups and the branching index (BI) had a significant correlation with TSI. This was corroborated from the TSI trends of the surrogate mixtures. The final ANN model had a single hidden layer with ten neurons and was arrived after 256 epochs of model training. 15% of the data was used for validation of the final ANN model and a regression coefficient ($R^2=0.97$) between the experimental and the predicted TSI was obtained. The model has an average absolute

error of 2.46 and in most cases, the error values are less than 2% of the experimentally measured value. The model can also be employed for predicting the TSI of real fuels provided the fuel functional groups are available.

Chapter 4:

Sooting propensity trends for diesel/gasoline-ether blends and their prediction using ANN.

The primary components of gasoline are paraffins, olefins, and aromatics, while diesel consists of paraffins, olefins, and naphthenes [135]. Despite the beneficial effects of paraffins on diesel fuel combustion quality, they tend to perform poorly at low temperatures. Aromatics and olefins in fuels can cause engine issues such as cleanliness problems, deposit formation, and the emission of carcinogenic or toxic substances, as well as contribute to ozone generation, all of which negatively affect engine performance. Therefore, additives such as metal deactivators, detergents, and antioxidants are often necessary to mitigate these issues in both gasoline and diesel fuels [136]. In addition, it is essential to address the tendency of fuels to produce soot, given its detrimental effects. Numerous approaches have been investigated, such as blending fossil fuels with alternatives that emit little or no particulate matter (PM), switching to cleaner fuel sources [10-14], and adopting cleaner combustion technologies [8, 9].

Various fuel characteristics, including oxygen concentration [137], aromatic content [138, 139], cetane number [138], and octane values [138], influence PM generation. In diesel fuel, properties such as high density, a high cetane number, and high energy content are typically preferred. Oxygenated compounds derived from renewable sources, such as biomass-based ethers and alcohols, have shown promise in reducing PM emissions [137, 140-142]. Experimental findings indicate that increasing a fuel's oxygen concentration leads to reduced PM emissions [137, 143]. Moreover, a

method for increasing oxygen concentration, known as leaner-lifted flame combustion (LLFC), has been shown to enable soot-free combustion of diesel fuel [144, 145]. However, it is important to note that while various oxygen functional groups can significantly impact cetane ratings, high oxygen content can decrease the fuel's energy content [24, 146]. Therefore, understanding these relationships is crucial for future fuel design.

The availability of oxygen in fuel affects PM emissions through two mechanisms: oxygen content and ignition chemistry. Soot-free combustion at sufficient oxygen levels is achieved by reducing soot formation in the diesel flame, which is influenced by the presence of oxygen downstream at the high-temperature point of combustion [147]. Fuel oxygen content reduces the extent of air and fuel mixing needed to achieve this effect [144, 148]. Additionally, the chemical nature of oxygenated molecules can influence combustion chemistry within the diffusive flame.

Several investigations, including theoretical, experimental, and modeling studies, have been conducted to better understand how the structure of oxygenated fuels affects soot emissions. For example, Mueller et al. [149] evaluated two oxygenates—tri(propylene glycol) methyl ether (TPGME) and dibutyl maleate (DBM)—as alternative diesel fuels for their soot-reducing benefits. Chemical kinetic reaction mechanisms for oxygenates and diesel fuel have also been studied by Westbrook et al. [150]. These studies found that oxygenates inhibit soot formation based on the recognized amounts of soot precursors, with variations in reaction mechanisms attributed to differences in the chemical structures of the oxygenates. In summary, soot formation in diesel fuel occurs due to premixed ignition, followed by quenching of

combustion due to insufficient oxygen to sustain it, resulting in soot burning in a diffusion flame.

Several experimental techniques, including smoke point (SP), soot capacity index, and mass fraction measurements, have been developed to assess the sooting tendencies of both premixed and diffusion flames [45, 85, 105, 151]. The smoke point, defined as the height of the flame from burning fuel in a wick-fed lamp without soot formation, has been particularly useful in studying diffusion flames [31]. The threshold sooting index (TSI) was introduced to quantify the sooting tendency of fuels, with various types of burners employed by different research groups to measure the SP required for calculating TSI [45].

To investigate the effects of oxygenates with various functional groups on sooting propensity, Barrientos et al. measured the smoke points of fuel blends composed of a base fuel and 40 target compounds using TSI [30]. However, it was argued that TSI inappropriately includes oxygenated fuels, as it is normalized by molecular weight and does not account for the effect of oxygen on reducing the air entrainment required for stoichiometric combustion. To address this, the oxygen-extended sooting index (OESI) was proposed as a new metric that incorporates the effect of fuel-borne oxygen by normalizing for the oxygen required for stoichiometric combustion. The calculation of OESI is as follows:

$$OESI = A \left(c + \left[\frac{h}{4} \right] - \left[\frac{o}{2} \right] \right) / SP + B \quad \dots\dots\dots[4.1]$$

where A and B represent the experimental setup, and *c*, *h*, and *o* represent the number of carbon, hydrogen, and oxygen atoms in the fuel molecule, respectively. The calculation of OESI accounts for these atoms and has been found suitable for evaluating

the sooting tendencies of hydrocarbons, oxygenates, and their blends. In this study, the effects of additives were examined, specifically five ethers: dibutyl ether (DBE), diethyl ether (DEE), diphenyl ether (DPE), dioctyl ether (DOE), and methyl tert-butyl ether (MTBE), when added to commercial gasoline (91) and diesel at various percentages (1%, 5%, 10%, and 20%) on the sooting tendencies of gasoline/diesel-ether blends. Additionally, AI models were developed to predict the sooting tendencies of these blends.

Table 8: Chemical structures of tested compounds

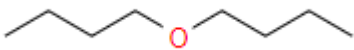
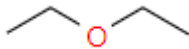
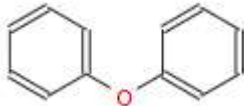
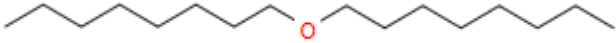
Name	abbreviation	Formula	Structure
dibutyl ether	DBE	$C_8H_{18}O$	
diethyl ether	DEE	$C_4H_{10}O$	
diphenyl ether	DPE	$C_{12}H_{10}O$	
Dioctyl ether	DE	$C_{16}H_{34}O$	
Methyl tert-butyl ether	MTBE	$C_5H_{12}O$	
Gasoline (91)	G		$\approx 4-12C$ (86% C & 14% H)
Diesel	D		$\approx 12-20 C$ (86% C & 14% H)

Table 9: Properties of tested compounds

compounds	MW (kg/kmol)	BP (°C)at 1 atm	Oxygen (wt%)	Density (kg/m ³)	Molar ratio (H/C)	molar ratio (O/C)
DBE	130.23	141	12.3	770	2.25	0.125
DEE	74.12	34.6	21.6	713.4	2.5	0.25
DPE	170.21	258.55	9.4	1080	0.83	0.083
DE	242.44	286- 287	6.6	806	2.125	0.063
MTBE	88.150	55.2	18.2	740.4	2.4	0.2
G	100	30– 210°C [1]	0	750	2	0
D	168	170- 360°C [2]	0	850	2	0

4.1 EXPERIMENTAL WORK

4.1.1 Chemicals

n-Heptane (used for cleaning), along with toluene and isooctane (used for calibration of the SP lamp), each with a purity of $\geq 99.5\%$, were obtained from Sigma-Aldrich

4.1.2 Fuels

The oxygenates (dibutyl ether, diethyl ether, diphenyl ether, dioctyl ether, and methyl tert-butyl ether (MTBE)) were obtained from Sigma Aldrich, each with a purity of $\geq 99\%$. The base fuels (diesel and gasoline 91) were sourced from gasoline and diesel

stations in Dhahran, Kingdom of Saudi Arabia, specifically selected for the current study, and their features are detailed in Tables 8 and 9, respectively.

4.1.3 Approach

The SP lamp specified by the ASTM method (D1322) from Kohler Company was used in the experiments, which were conducted strictly in accordance with ASTM D1322. Flame height was controlled by adjusting the wick length. Each experimental run of a fuel blend was repeated three times to ensure that the variation in SP readings did not exceed 1 mm. The uncertainty in the SP measurements reported here is approximately 0.5 mm. Two standard reference fuel blends, isooctane/toluene (60/40 and 80/20 vol%), were used to calibrate the SP measurements as per ASTM D1322. Smoke points were measured at atmospheric pressure (1 atm) and room temperature (24 °C). It was also confirmed that environmental conditions (relative humidity and ambient temperature) did not affect the SP measurements.

4.2 Results and discussions

Fuel blend sooting propensities have been explored and predicted using the TSI mixing rule [67]. However, TSI alone is insufficient for blends containing oxygenates, so the OESI is proposed [28]. Therefore, the experimental findings are discussed in terms of SP [152], TSI [101], and OESI. Although indexed data (SP, TSI, and OESI) may not exhibit a fully linear relationship with the volume fraction of oxygenated compounds, reliable predictions of SP, TSI, and OESI can be expected due to the use of Artificial Neural Network (ANN) models for prediction.

4.2.1 Model constants

In this study, the model constants for TSI, represented as "a" and "b," and for OESI, represented as "A" and "B," were calculated using the reference compounds toluene and isooctane. The average SPs of isooctane and toluene were measured as 42 mm and 5 mm, respectively. To calculate the TSI equation constants (a and b), TSIs of 6.4 and 44 were used for isooctane and toluene, respectively, obtained from the source [76]. For OESI, values of 6.8 and 46.1 for isooctane and toluene, respectively, were taken from the reference [33] to calculate the constants A and B. The derived model constants were $a = 2.4$ and $b = -0.066$ for TSI, and $A = 26.2$ and $B = -1.06$ for OESI. These constants were applied in the study.

4.2.2 Sooting Indices for Diesel/Gasoline-Oxygenates Blends

SP measurements of binary blends were conducted using an SP lamp for two sets. The first set included diesel with various oxygenates (dibutyl ether, diethyl ether, diphenyl ether, dioctyl ether, and methyl tert-butyl ether) at different volume percentages (1%, 5%, 10%, and 20%). The second set used gasoline in place of diesel. The measured SP, TSI, and OESI data are provided in Table 11. This chapter primarily focuses on TSI and OESI; however, the impact of oxygenates on the SPs of gasoline and diesel is illustrated in Figure 14b.

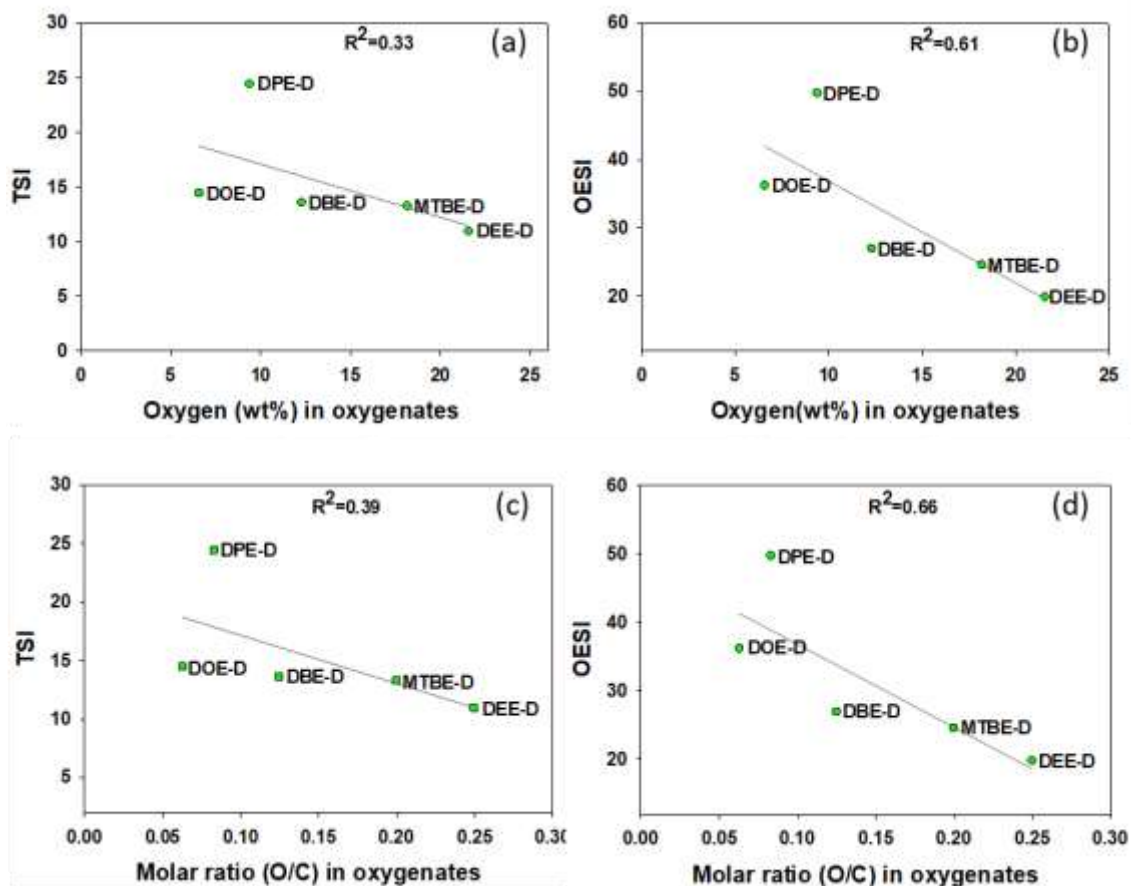


Figure 35: TSI and OESi of 20 vol% oxygenates in 80 vol% diesel blends, including diethyl ether-diesel (DEE-D), dioctyl ether-diesel (DOE-D), diphenyl ether-diesel (DPE-D), dibutyl ether-diesel (DBE-D), and methyl tert-butyl ether-diesel (MTBE-D), are plotted against the oxygen content (wt%) and the molar ratio (O/C) of the oxygenates. Panels (a) and (c) display the TSI, while panels (b) and (d) show the OESi.

Figure 35 illustrates the impact of oxygenates on the TSI and OESi indices. Compared to TSI, the OESi of oxygenate-diesel blends shows stronger correlations with both oxygen content (O wt%) and the molar ratio of oxygen to carbon (O/C) in the oxygenates. The R^2 values for the correlations with oxygen weight percentage and the

O/C ratio were 0.33 and 0.39 for TSI, and 0.71 and 0.75 for OESI, respectively. This aligns with the known influence of oxygenates on particulate matter (PM) emissions [137, 149, 150] and reinforces that OESI is a more suitable indicator of oxygenates' sooting propensity than TSI [33]. Consequently, both TSI and OESI were used to interpret sooting trends.

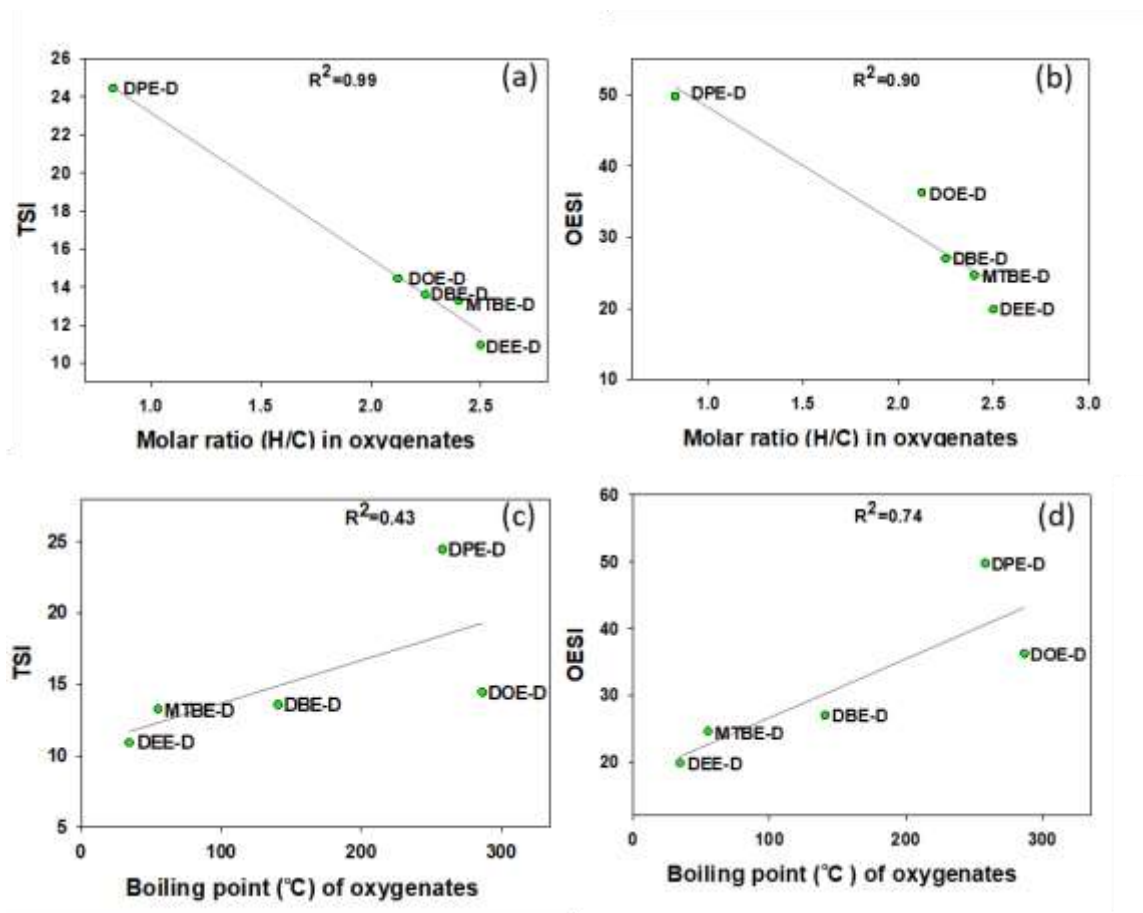


Figure 36:

TSI(a & c) and OESI(b & d) of 20 vol% oxygenates-80 vol% diesel blends (diethyl ether-diesel (DEE-D), dioctyl ether-diesel (DOE-D), diphenyl ether-diesel (DPE-D), dibutyl ether-diesel (DBE-D), and methyl tert-butyl ether-diesel (MTBE-D)) vs. molar ratio (H/C) and boiling point of oxygenates.

The TSI and OESI values are also correlated with the molar ratio of hydrogen to carbon (H/C) and the boiling point of the oxygenates, as demonstrated in Figure 36. The TSI

exhibits a strong inverse relationship with the hydrogen-to-carbon ratio, shown in Part A of this figure. The diesel blend with the lowest hydrogen-to-carbon ratio (0.83), diphenyl ether (DPE), displayed the highest sooting tendency (TSI: 24) when blended as DPE20D80 (20% diphenyl ether and 80% diesel). Conversely, diethyl ether, with the highest H/C ratio (2.5), resulted in the lowest sooting tendency (TSI: 11) at the same blend ratio, as seen in Part A of Figure 36. A similar trend appears in Part B for the OESI of these two blends. Thus, as the hydrogen-to-carbon ratio increases, the sooting tendencies indicated by TSI and OESI decrease. In Figure 36, Parts C and D, the opposite trend emerges between sooting tendency indices (TSI, OESI) and the boiling point of pure oxygenates. Therefore, when selecting ethers for blending with diesel to reduce sooting, both the hydrogen-to-carbon ratio and the boiling point of the oxygenates should be considered.

Regarding the density and molecular weight of oxygenates, the relationships between these two features (density and molecular weight) and the sooting tendency indices (TSI and OESI) are proportional, as shown in Figure 37.

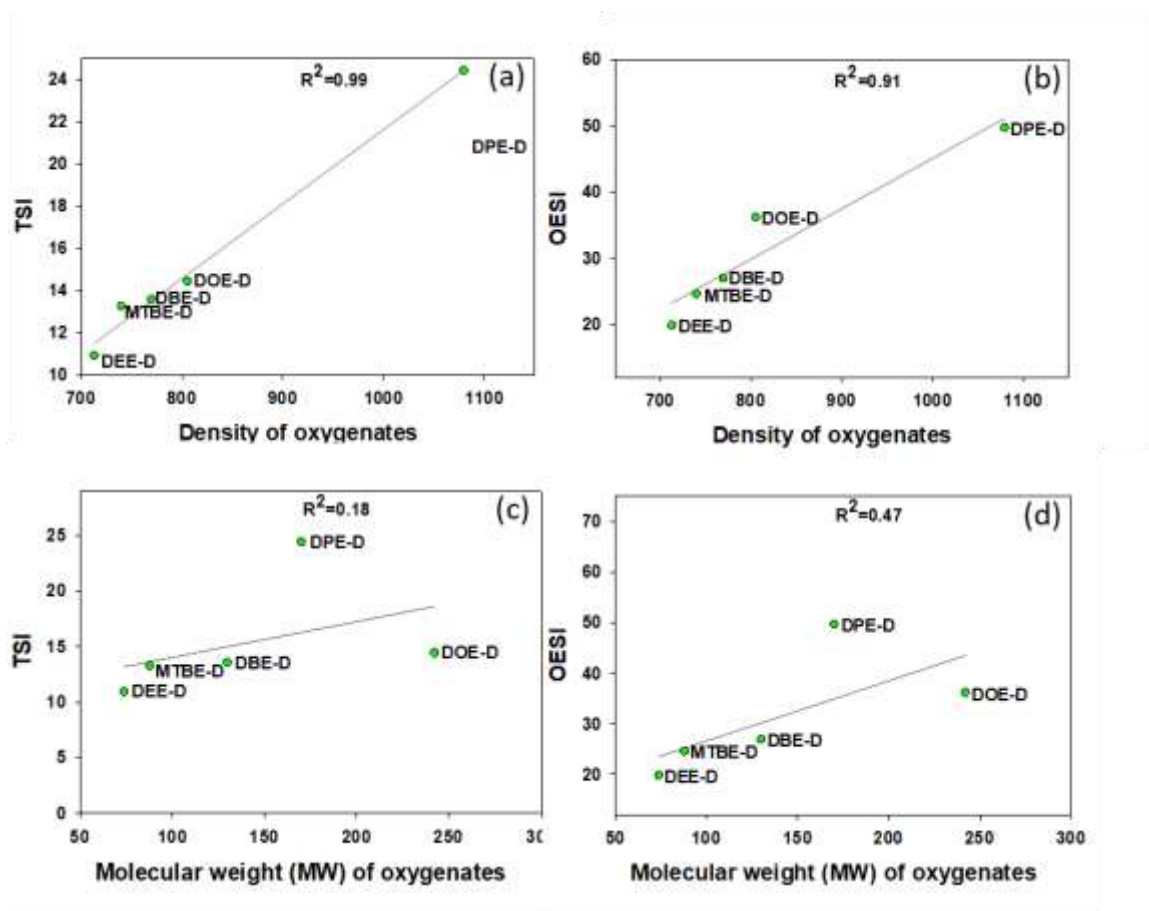


Figure 37: The TSI (a and c) and OESi (b and d) of blends containing 20 vol% oxygenates (diethyl ether-diesel (DEE-D), dioctyl ether-diesel (DOE-D), diphenyl ether-diesel (DPE-D), dibutyl ether-diesel (DBE-D), and methyl tert-butyl ether-diesel (MTBE-D)), in relation to the density and molecular weight of the oxygenates.

4.2.3 Blending the base fuel and oxygenates.

The oxygenates are typically blended with a base fuel, usually composed of hydrocarbons, at specific compositions to assess their sooting propensity in liquid fuels. For example, prior studies [30, 33] have used different oxygenate-hydrocarbon base fuels, such as 65 vol% n-heptane and 35 vol% toluene, to provide a wide range of oxygen content. These studies demonstrate that the TSI consistently decreases as the

oxygen mass fraction increases. Given that oxygenates often have low sooting propensities, the base fuel should contain a certain percentage of aromatics to accurately measure the SP using this technique. However, findings from this approach may be confounded, as the percentage of toluene decreases as oxygen is added, while maintaining a constant *n*-heptane-to-toluene ratio. Aromatic hydrocarbons, like toluene, have the highest sooting propensity among components found in base fuels (gasoline and diesel), as shown in sooting propensity evaluations [30, 45, 153].

In this study, oxygenates (ethers) were directly added to gasoline or diesel (instead of *n*-heptane and toluene) at constant volume fractions. Five compounds—dibutyl ether (DBE), diethyl ether (DEE), diphenyl ether (DPE), dioctyl ether (DOE), and methyl tert-butyl ether (MTBE)—were blended with a base fuel (Gasoline 91 or Diesel) at 1%, 5%, 10%, and 20% volume fractions to examine the factors influencing their sooting tendencies. This approach resulted in forty blends, with each oxygenated compound tested in four blends for both diesel and gasoline to observe sooting trends. Here, the sooting tendencies of only ether-based fuel blends, using TSI and OESI indices, are discussed, as previous work addressed the sooting tendencies of oxygenated compounds (alcohol and ether) using only the SP index [152].

4.2.3.1 Gasoline blend

Figure 38a shows the TSI of blends of the five compounds with gasoline at volume fractions of 1%, 5%, 10%, and 20%. The TSIs of oxygenate-gasoline blends generally decrease as the oxygenate concentration increases, with the exception of the diphenyl ether (DPE)-gasoline blend. An increase in DPE in gasoline (91) leads to a higher sooting tendency of the blend, while the other oxygenates show the opposite effect.

These results can be explained by the parameters of the oxygenates in Tables 8 and 9, as well as the functional groups listed in Table 10.

Both diethyl ether (DEE) and dibutyl ether (DBE) similarly affect gasoline's sooting tendency. As shown in Figure 38a, the TSI of gasoline-DEE and gasoline-DBE blends decreases from around 15 to approximately 9 and from 12 to 8, respectively, as DEE and DBE volume fractions increase from 1 to 20 vol%. This small difference in sooting tendency reduction between DEE and DBE is due to their largely similar properties: they both have a branching index of 0, molar H/C ratios of 2.25 (DBE) and 2.5 (DEE), densities of 770 kg/m³ (DBE) and 713 kg/m³ (DEE), and comparable functional group distributions (paraffinic CH₃, paraffinic CH₂, paraffinic CH, olefinic, naphthenic, and aromatic groups as shown in Table 10) aside from ether O groups. However, they differ in properties such as the molar O/C ratio (0.125 for DBE and 0.25 for DEE), molecular weight (130 for DBE and 74 for DEE), oxygen content (12.3 wt% for DBE and 21.6 wt% for DEE), and boiling point (141°C for DBE and 35°C for DEE). These distinctions suggest that each factor listed in Table 9 contributes to TSI reduction in oxygenated fuels, though with varying degrees of influence.

These differences in the mentioned factors indicate that the impact of DEE on the sooting tendency reduction of the gasoline blend should be higher than that of the DBE with the same volume fraction. This can be obviously seen in Figure 38a, where the total reduction of the TSIs of gasoline-DEE and DBE blends is 6 and 3.5, respectively, as the volume percentages of DEE and DBE increase from 1 to 20. However, DEE and DBE approximately reduce TSIs of gasoline blends to the same level (9). Therefore, OESI was used, as shown in Figure 38b, where using OESI to describe the sooting tendency of

oxygenates is better than TSI, as mentioned earlier. The OESI reduction of DEE and DBE-gasoline blends is 11 and 9, respectively, with increasing volume fraction from 0.1 to 0.2, leading to a reduced OESI of DEE and DBE blends from 27 to 16 and from 28 to 19, respectively. This can be explained by the oxygen factor included in the OESI equation (2), as well as H and C. Also, this is consistent with other factors mentioned above.

Dioctyl ether (DOE) and methyl tert-butyl ether (MTBE) have a relatively smaller impact on the sooting tendency of gasoline compared to the other compounds in this study. This is due to their feature values, shown in Table 9, which fall between those of DBE, DEE, and DPE. The TSI values for DOE- and MTBE-gasoline blends decrease from around 16 to about 11 as DOE and MTBE content increases from 1% to 20% by volume, as depicted in Figure 38a, despite some variation in their properties. Therefore, OESI was employed to more effectively differentiate their sooting tendencies, as shown in Figure 38b. The OESI reduction for the MTBE-gasoline blend is higher than that of the DOE-gasoline blend, consistent with the characteristics of DOE and MTBE discussed and listed in Tables 8 and 9.

On the other hand, DPE, classified as an aromatic compound, contains two benzene rings that make up approximately 90% of its molecular weight (170), as shown in Table 8. In Figure 38a, the TSI of the DPE-gasoline blend increases from around 16 to about 28 as the aromatic functional groups rise from approximately 5% to 27% by weight, due to the addition of DPE to gasoline from 1% to 20% by volume, as shown in Table 11. This finding

aligns with numerous studies [238, 204-64] that report aromatics as significantly increasing the sooting tendency of fuel.

This behavior is attributed to DPE having the highest density (1080 kg/m^3) among the oxygenates (ethers), the lowest molar ratio of H/C (0.83), as shown in Table 9, and the highest branching index (BI) (2), which indicates the size and position of the branched functional groups (CH_3 and CH_2) relative to the longest carbon chain, as detailed in Table 10. For more information on BI, readers are referred to the work of [79]. These factors—aromaticity, branching, and the features listed in Tables 9 and 10—explain the observed increase in the sooting tendency of gasoline as the DPE content rises from 1% to 20% by volume. A similar trend was observed in the OESI values for DPE-gasoline blends, as shown in Figure 38b, driven by the same underlying reasons. Further insights into the impact of DPE on sooting tendencies are discussed in the section on aromatic effects, where additional evidence is presented to support the conclusion that DPE enhances the aromatic content in gasoline and diesel, thereby increasing soot formation

Table 10: Functional groups and Branched Index (BI) of fossil and oxygenated (pure and blends) fuels

Ethers and blends in vol%	P.CH ₃ (wt%)	P.CH ₂ (wt%)	P.CH (wt%)	Olef (wt%)	Naph (wt%)	Arom (wt%)	Ether O wt%	Mol Wt	BI
Gasoline (91)	60.9	15.9	3.3	2.3	13.1	3.8	0.0	100.0	0.5
Diesel	20.8	54.2	11.7	0.0	8.2	5.1	0.0	168.0	0.5
Diphenyl ether(DPE)	0.0	0.0	0.0	0.0	0.0	90.6	9.4	170.0	2.0
Diocetyl ether(DOE)	12.4	81.0	0.0	0.0	0.0	0.0	6.6	242.4	0.0
Diethyl ether(DEE)	40.5	37.8	0.0	0.0	0.0	0.0	21.6	74.0	0.0
Methyl tert-butyl ether(MTBE)	68.2	0.0	0.0	0.0	0.0	0.0	18.2	88.0	0.5
Dibutyl ether(DBE)	23.1	64.6	0.0	0.0	0.0	0.0	12.3	130.0	0.0
1% DPE+ 99% gasoline	60.1	15.7	3.3	2.3	12.9	5.0	0.1	100.6	0.5
5% DPE+ 95% gasoline	56.7	14.8	3.1	2.1	12.2	9.8	0.7	103.0	0.6
10% DPE+ 90% gasoline	52.6	13.8	2.9	2.0	11.3	15.7	1.3	106.0	0.6
20% DPE+ 80% gasoline	44.9	11.7	2.5	1.7	9.6	26.6	2.5	112.2	0.8
1%DOE+ 99% gasoline	60.4	16.6	3.3	2.3	12.9	3.7	0.1	100.6	0.5
5%DOE+ 95% gasoline	58.3	19.4	3.2	2.2	12.4	3.6	0.4	103.2	0.5
10%DOE+ 90% gasoline	55.8	22.9	3.0	2.0	11.7	3.4	0.7	106.7	0.5
20%DOE+ 80% gasoline	50.7	29.7	2.6	1.8	10.3	3.0	1.4	114.2	0.5
1% DEE+99% gasoline	60.7	16.1	3.3	2.3	12.9	3.7	0.2	99.7	0.5
5% DEE+95% gasoline	60.0	17.0	3.2	2.2	12.5	3.6	1.0	98.4	0.5
10% DEE+90% gasoline	59.0	18.0	3.0	2.1	11.8	3.4	2.1	96.8	0.4
20% DEE+80% gasoline	57.0	20.1	2.7	1.8	10.6	3.0	4.2	93.7	0.4
1%MTBE+99% gasoline	61.0	15.8	3.3	2.3	12.9	3.7	0.2	99.9	0.5
5%MTBE+95% gasoline	61.3	15.2	3.2	2.2	12.4	3.6	0.9	99.3	0.5
10%MTBE+90% gasoline	61.6	14.4	3.0	2.1	11.8	3.4	1.8	98.7	0.5
20%MTBE+80% gasoline	62.4	12.8	2.7	1.8	10.5	3.0	3.6	97.4	0.5
1%DBE+99% gasoline	60.5	16.4	3.3	2.3	12.9	3.7	0.1	100.2	0.5
5%DBE+95% gasoline	59.0	18.4	3.2	2.2	12.4	3.6	0.6	101.2	0.5
10%DBE+90% gasoline)	57.1	20.9	3.0	2.1	11.7	3.4	1.3	102.4	0.5
20%DBE+80% gasoline	53.2	25.8	2.7	1.8	10.4	3.0	2.5	104.9	0.4
1% DPE+ 99% diesel	20.5	53.6	11.5	0.0	8.1	6.2	0.1	168.0	0.5
5% DPE+ 95% diesel	19.5	50.9	10.9	0.0	7.7	10.4	0.6	168.1	0.6
10% DPE+ 90% diesel	18.2	47.6	10.2	0.0	7.2	15.6	1.2	168.2	0.7
20% DPE+ 80% diesel	15.8	41.2	8.9	0.0	6.3	25.6	2.3	168.5	0.9
1%DOE+ 99% diesel	20.7	54.5	11.6	0.0	8.2	5.1	0.1	168.5	0.5
5%DOE+ 95% diesel	20.4	55.5	11.1	0.0	7.9	4.9	0.3	170.5	0.5
10%DOE+ 90% diesel	20.0	56.8	10.6	0.0	7.5	4.6	0.6	173.1	0.5
20%DOE+ 80% diesel	19.2	59.4	9.4	0.0	6.7	4.1	1.3	178.5	0.4
1% DEE+99% diesel	20.9	54.1	11.6	0.0	8.2	5.1	0.2	166.2	0.5
5% DEE+95% diesel	21.6	53.5	11.2	0.0	7.9	4.9	0.9	159.4	0.5
10% DEE+90% diesel	22.4	52.8	10.7	0.0	7.5	4.7	1.8	151.6	0.4
20% DEE+80% diesel	24.2	51.4	9.6	0.0	6.8	4.2	3.7	137.7	0.3
1%MTBE+99% diesel	21.2	53.8	11.6	0.0	8.2	5.1	0.2	166.7	0.5
5%MTBE+95% diesel	22.8	51.9	11.2	0.0	7.9	4.9	0.8	161.6	0.5
10%MTBE+90% diesel	24.9	49.5	10.6	0.0	7.5	4.7	1.6	155.5	0.5
20%MTBE+80% diesel	29.2	44.5	9.6	0.0	6.8	4.2	3.2	144.5	0.5
1%DBE+99% diesel	20.8	54.3	11.6	0.0	8.2	5.1	0.1	167.6	0.5
5%DBE+95% diesel	20.9	54.7	11.1	0.0	7.9	4.9	0.6	165.8	0.5
10%DBE+90% diesel	21.0	55.2	10.6	0.0	7.5	4.7	1.1	163.7	0.4
20%DBE+80% diesel	21.2	56.1	9.5	0.0	6.7	4.2	2.3	159.4	0.4

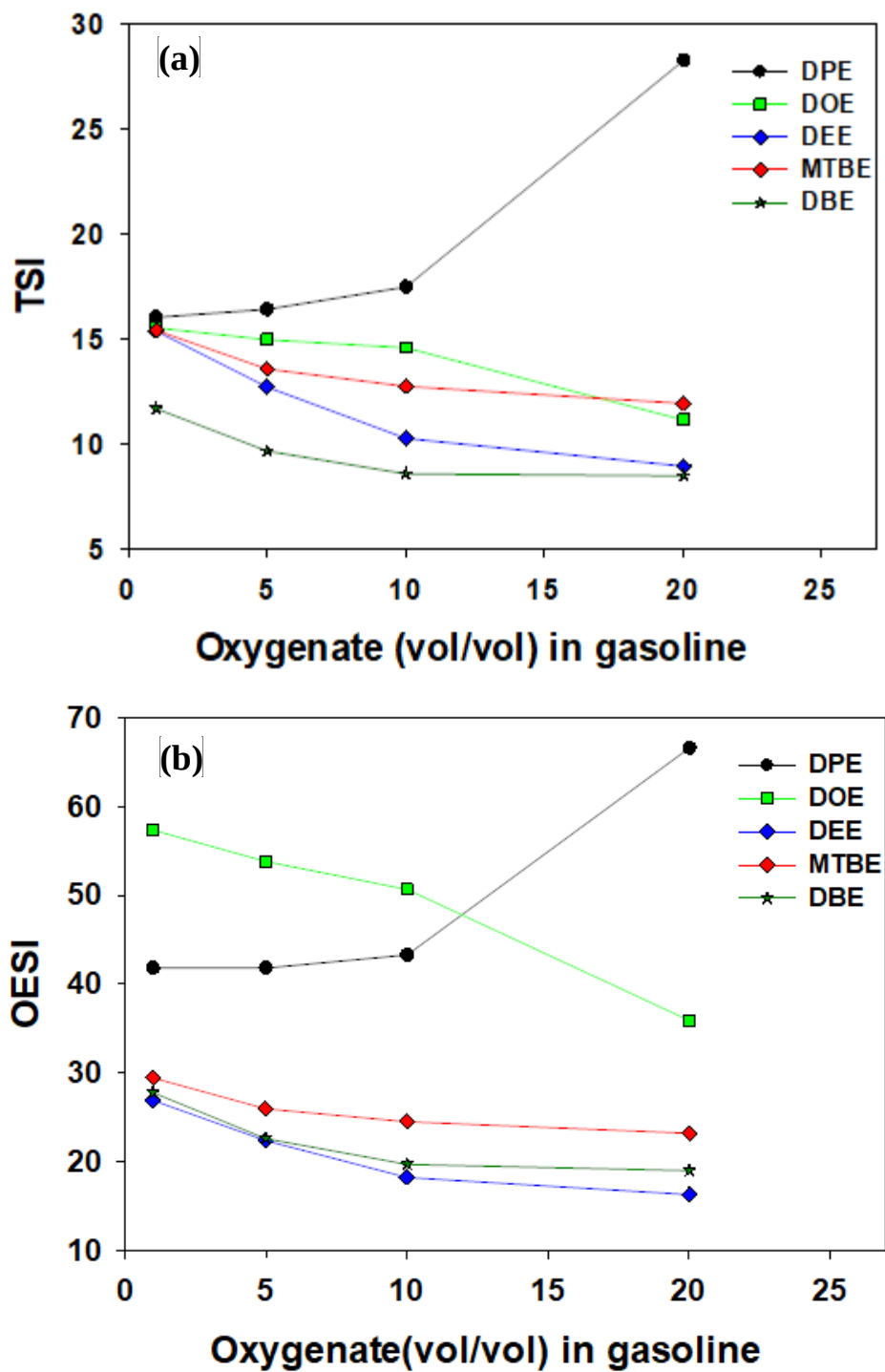


Figure 38: Values of (a)TSI and (b) OESi for gasoline (91)-ethers blends.

4.2.3.2 Diesel blend

The trends of TSIs for oxygenates-diesel blends are largely similar to those observed for gasoline blends, with slight differences, as depicted in Figure 39a. In general, the reduction in TSIs for oxygenates-diesel blends is less pronounced than for gasoline blends. For instance, the TSI reduction for MTBE-diesel is 13, compared to 11 and 8 for DOE-gasoline and DBE-gasoline, respectively. Similarly, the TSI of DEE-diesel reduces to 11, whereas that of DEE-gasoline reduces further to 9. In contrast, the TSI of DPE-diesel increases to 24, while the TSI of DPE-gasoline rises to 28.

This variation can be attributed to the differing chemical compositions of gasoline and diesel. Gasoline typically contains hydrocarbons with 4 to 12 carbon atoms, whereas diesel comprises hydrocarbons with 8 to 21 carbon atoms. Since diesel generally has a higher number of carbon atoms than gasoline, its sooting tendency is naturally higher. These observations align with the factors listed in Table 9 and the results discussed above.

Regarding the OESIs of oxygenates-diesel blends, shown in Figure 39b, the trends are similar to those of oxygenates-gasoline blends, with a greater reduction in OESIs for gasoline blends, excluding the DPE blend. This can be attributed to the same reasons previously discussed for TSI reduction. Since DPE is classified as an aromatic compound with two rings, its addition increases aromaticity while inversely decreasing the paraffinic CH₂ groups, leading to a higher sooting tendency [152].

When DPE is added to the blend, the weight percentage of CH₂ functional groups—which play a role in reducing sooting tendency by enhancing combustion [101, 152],—decreases to 12% and 41% for gasoline and diesel blends, respectively. Consequently, the reduction in the sooting tendency of the gasoline blend (OESI = 67)

is less significant than that of the diesel blend (OESI = 50) when 20 vol% DPE is added, despite the stronger effect of aromatics compared to CH₂ groups.

Comparing the TSIs and OESIs of oxygenates-diesel blends reveals similar trends; however, the OESI values provide a more accurate representation, as they highlight the differences among the diesel blends. These differences reflect the significant variations in the properties of the oxygenates, particularly between DPE (OESI = 50, TSI = 24) and DEE (OESI = 20, TSI = 11), as shown in Figure 39b. This underscores why OESI is the preferred metric for describing the sooting tendency of oxygenates.

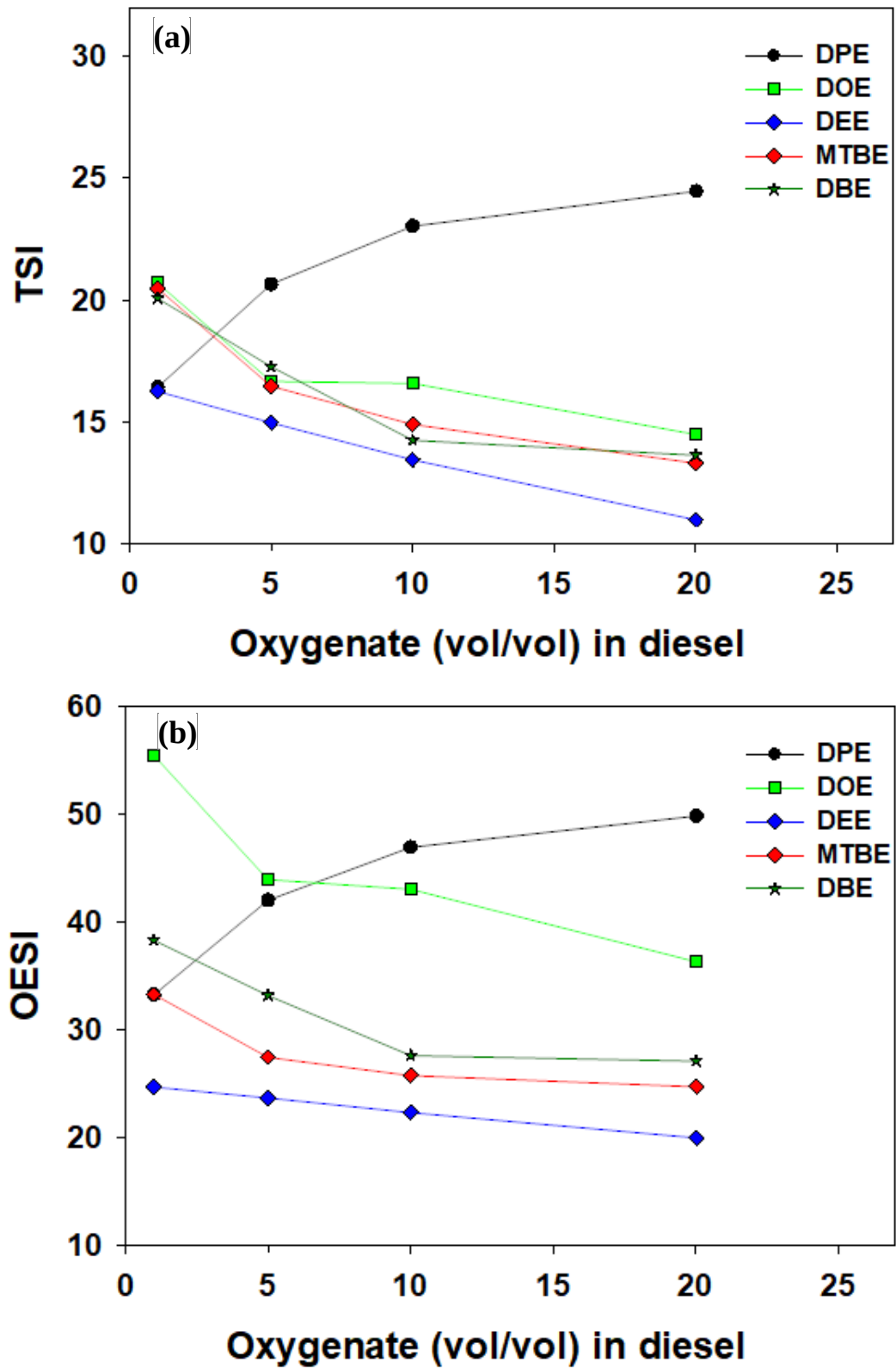


Figure 39: Values of (a)TSI and OESi(b) for Diesel -ethers blends.

4.3 Aromatics' effect

Aromatic compounds have long been recognized as significant precursors to soot formation in combustion processes [76, 154-156]. The presence of aromatics in fuels has been shown to increase the sooting tendency, which contributes to various environmental and health concerns [101, 152].

The influence of aromaticity on the sooting propensity of fuels is explored in this discussion. Several factors, including chemical composition, molecular structure, and combustion conditions, affect a fuel's sooting tendency. Aromaticity is one of the most significant contributors to this phenomenon [156]. The ring structure of aromatic molecules, characterized by alternating double bonds, imparts stability to the molecule, making it resistant to disintegration during combustion [109]. Consequently, large polycyclic aromatic hydrocarbons (PAHs), which are well-established precursors of soot particles, are formed during the combustion process [157].

Numerous studies [158-161] have explored the influence of aromaticity on sooting tendencies. Christopher P. et al. demonstrated that fuels with a higher aromaticity index (AI) exhibit a greater propensity for soot formation [162]. Similarly, Qasem M.A.A. et al. confirmed that increasing aromaticity in fuels results in higher soot production during combustion [101, 152].

Additional investigations have examined the role of specific aromatic compounds in soot formation [30, 101, 152, 163]. Research by Paul et al. and Qasem M.A.A. et al. revealed that aromatic compounds with a greater number of rings and a higher degree

of substitution exhibit a significantly higher sooting propensity. Polycyclic aromatic hydrocarbons (PAHs) exhibit a significantly higher sooting propensity compared to monocyclic aromatic hydrocarbons (MAHs) [163].

In this study, diphenyl ether (DPE) was investigated as a representative aromatic compound to evaluate its impact on the sooting tendency of gasoline and diesel fuels. DPE was chosen due to its strong aromaticity and the presence of two benzene rings, which account for approximately 90% of its molecular mass. This makes DPE a preferred oxygenated fuel for studying the sooting behavior of aromatic compounds. Aromatic compounds, such as DPE, are known to substantially influence the sooting tendency of fuels.

Additionally, DPE possesses unique properties that contribute to its higher sooting tendency compared to other oxygenates (ethers) studied. It has the highest density (1080 kg/m^3), the lowest molar H/C ratio (0.83), and the highest branching index (BI), which reflects the size and position of branching functional groups along the longest carbon chain. These factors make DPE an ideal molecule for examining the sooting behavior of aromatics in fuel blends.

The study found that the TSI and OESI of fuel blends containing DPE increased with the volume percentage of DPE. For example, the TSI and OESI of the DPE-gasoline blend rose from 16 to 28 and 42 to 67, respectively, as the DPE volume increased from 1% to 20%. Similarly, for the DPE-diesel blend, the TSI increased from 16 to 24, and the OESI rose from 33 to 50. These findings align with existing literature and confirm that the sooting tendency of fuel blends increases as the volume percentage of DPE increases.

Notably, OESI values provided more meaningful insights compared to TSI values, particularly due to the significant differences observed as the DPE volume increased. This can be attributed to the representation of oxygen content in the OESI calculation (Equation 2), as discussed earlier.

The emissions of DPE-diesel blends have been explored in the literature using diesel engines with varying DPE concentrations [164-166]. Studies have indicated that DPE increases CO emissions [167]. This is attributed to the higher oxygen content introduced by the additive, which lowers the local fuel richness during combustion—the primary source of CO emissions.

Srihari et al. reported that the greater oxygen content in DPE blends promotes the oxidation of CO to CO₂, resulting in elevated CO₂ emissions [164]. Furthermore, increasing the concentration of DPE in diesel blends tends to raise NO_x emissions. This is due to the additional oxygen availability during combustion, which elevates the temperature and subsequently increases NO_x formation [164].

The higher density of DPE also contributes to its combustion behavior. It reduces flowability, causing some of the additive to deposit at the combustion chamber's exit. These deposits are inadvertently burned at high temperatures and transported through the exhaust, resulting in soot particle emissions [167]. Sulfur in diesel further exacerbates smoke formation by reacting with these deposits to form sulfates [167].

To mitigate NO_x emissions, antioxidant additives are recommended, as they lower the flame temperature and reduce NO_x formation [164]. Reducing aromatic content in fuels also decreases flame temperatures, resulting in lower NO emissions [167]. Since aromatic compounds have high carbon-to-hydrogen ratios, fuels with reduced aromatic

content produce more water and less carbon dioxide compared to fuels with higher aromatic levels [167].

These findings align with our results. However, previous studies, such as those by [167] did not explicitly measure the smoke generated during combustion. To address this gap, we employed the SP Lamp apparatus—a straightforward and reliable tool—to measure smoke emissions effectively.

The smoke point (SP) was measured using the SP Lamp. The SPs of DPE-gasoline blends were 15, 15, 14.5, and 9.5 mm at DPE loads of 1, 5, 10, and 20% vol, respectively. Similarly, the SPs of DPE-diesel blends were 24.5, 19.5, 17.5, and 16.5 mm at the same loads. These measurements resulted in TSI values for DPE-gasoline blends of 16, 16, 17, and 28, respectively, and OESI values of 41, 41, 43, and 67, respectively. For DPE-diesel blends, the TSI values were 16, 21, 23, and 24, respectively, while the OESI values were 33, 42, 47, and 50, respectively. These results, particularly the OESI values, align with the previously discussed reasons and literature, indicating that the sooting tendency of the blends increased with higher percentage volumes of DPE.

In summary, the presence of aromatic compounds, including diphenyl ether (DPE), in fuels increases their sooting tendency and emissions harmful to both humans and the environment during combustion, as demonstrated in the DPE-gasoline and diesel blends. This occurs because aromatic compounds resist decomposition, leading to the formation of large PAHs and ultimately soot particles. Further research is needed to develop techniques for reducing fuel sooting propensity and to better understand the mechanisms of soot formation from aromatic compounds.

4.4 PREDTION of SP, TSI and OESi using ANN.

4.4.1 Methodologies

4.4.1.1Dataset

A collection of 40 fuel samples was used in this study, 20 of which were mixtures of oxygenated gasoline and diesel. The dataset used in this article was specifically generated for this research. All relevant information, including mixture compositions, SP, TSI, and OESI values, is provided in Table 11.

Table 11: SP, TSI, and OESi of mixtures

Ethers+gasoline /diesel blends in vol%	SP	TSI	OESi
1% DPE+ 99% gasoline	15	16.0	41.7
5% DPE+ 95% gasoline	15	16.4	41.7
10% DPE+ 90% gasoline	14.5	17.5	43.2
20% DPE+ 80% gasoline	9.5	28.3	66.5
1%DOE+ 99% gasoline	15.5	15.5	57.3
5%DOE+ 95% gasoline	16.5	15.0	53.7
10%DOE+ 90% gasoline	17.5	14.6	50.6

20%DOE+ 80% gasoline	24.5	11.1	35.8
1% DEE+99% gasoline	15.5	15.4	26.8
5% DEE+95% gasoline	18.5	12.7	22.3
10% DEE+90% gasoline	22.5	10.3	18.2
20% DEE+80% gasoline	25	8.9	16.2
1%MTBE+99% gasoline	15.5	15.4	29.4
5%MTBE+95% gasoline	17.5	13.6	25.9
10%MTBE+90% gasoline	18.5	12.7	24.4
20%MTBE+80% gasoline	19.5	11.9	23.1
1%DBE+99% gasoline	20.5	11.7	27.7
5%DBE+95% gasoline	25	9.6	22.5
10%DBE+90% gasoline	28.5	8.6	19.6

20%DBE+80% gasoline	29.5	8.5	18.9
1% DPE+ 99% diesel	24.5	16.4	33.2
5% DPE+ 95% diesel	19.5	20.6	41.9
10% DPE+ 90% diesel	17.5	23.0	46.8
20% DPE+ 80% diesel	16.5	24.4	49.8
1%DOE+ 99% diesel	19.5	20.7	55.4
5%DOE+ 95% diesel	24.5	16.6	43.9
10%DOE+ 90% diesel	25	16.5	43.0
20%DOE+ 80% diesel	29.5	14.5	36.2
1% DEE+99% diesel	24.5	16.2	24.6
5% DEE+95% diesel	25.5	14.9	23.6
10% DEE+90% diesel	27	13.4	22.2
20% DEE+80% diesel	30	10.9	19.9
1%MTBE+99% diesel	19.5	20.4	33.2
5%MTBE+95% diesel	23.5	16.4	27.4
10%MTBE+90% diesel	25	14.9	25.7

20%MTBE+80% diesel	26	13.3	24.6
1%DBE+99% diesel	20	20.0	38.2
5%DBE+95% diesel	23	17.2	33.1
10%DBE+90% diesel	27.5	14.2	27.5
20%DBE+80% diesel	28	13.6	27.0

4.4.1.2 Input determination with functional groupings

The molecular composition of the blend was determined by examining the functional groups present in each of its molecules, as outlined in previous work [101, 152]. For example, in a blend comprising 20% diphenyl ether and 80% diesel by volume, the functional groups were as follows: 16 wt.% CH₃ paraffins, 41 wt.% CH₂ paraffins, 9 wt.% CH paraffins, 0 wt.% olefins, 6 wt.% naphthenes, 26 wt.% aromatics, and 2 wt.% ether oxygen. In some mixtures, including this one, the total weight percentage of the functional groups does not equal 100%. This discrepancy occurs because quaternary carbon atoms in the paraffinic family were excluded from this study due to their minor contribution and the difficulty of detecting them in petroleum fuels using ¹H NMR spectroscopy.

The Branching Index (BI) quantifies the degree of branching in molecules by numerically representing the size and location of methyl/methylene branching. Since neither group contains a carbon atom connected to the longest carbon chain, their BI values are zero. Weight percentage (wt%) rather than mole percentage (mol%) was

used to represent functional group presence to avoid over- or under-representation [79]. Fuel is typically represented and blended by volume fraction, with densities and blending ratios used to categorize functional groups in mixtures. Given its significant impact on the physical properties of fuels, molecular weight (MW) was selected as one of the 12 inputs for the proposed model. The average MW of each blend was determined based on blend compositions, with the MWs of 20 gasoline and 20 diesel samples calculated using a documented method [15]. A previous study [79] details the method used to derive the functional groups and BI of gasoline and diesel from their ^1H NMR spectra. Blend density was calculated using the following equation:

$$\text{Density(average)} = \text{density (compound 1)} * \text{vol\%} + \text{density (compound 2)} * \text{vol\%}$$

Finally, using the molecular weights of the compounds, two inputs for the molar ratios of O/C and H/C were calculated.

4.4.1.3 Development of ANN

The dataset was divided into training, validation, and test sets, with the training set comprising 70% of the data, and the validation and test sets each making up 15%. Training and validation were performed simultaneously. The total number of hidden layers, neurons, epochs, and the loss function were all determined using the validation set. The multilayer perceptron (MLP) was trained with backpropagation to build the ANN models. The test set was used to evaluate the ANN's performance after training and validation, with final evaluation based on its performance on the test set. Parameter optimization was carried out using MATLAB's NN tool. The validation set was specifically used for model validation before applying the test set.

During parameter tuning, several iterations (epochs) were conducted to minimize error for each ANN model. Each epoch represented a pattern of input data used in training. The final model was created using the optimal parameters, and after identifying the best topology, the ANN model was retrained, validated, and tested using appropriate test sets. Each dataset entry contained 12 inputs and one output (SP, TSI, or OESI) for each of the 40 data points. Figures 40, 41, and 42 show the Pearson correlation analysis results, illustrating the correlation between each input and output. As shown in these figures, aromatic C-CH groups and the Branching Index (BI) significantly influence TSI and OESI. However, nonlinear correlations between the 12 inputs and the single output may reveal additional findings, even when individual inputs appear insignificant.

To manage computational cost, parameters were examined individually across broad ranges of hyperparameters, with changes in one parameter while keeping related factors constant to maintain correlation. For instance, if adjusting the number of hidden layers, the outcome represented an average from testing different hidden neuron counts and epochs. Parameters were then sequentially adjusted until all were optimized. The mean absolute error was used as the loss function to assess model accuracy, and the code developed for this study is provided in the Appendix.

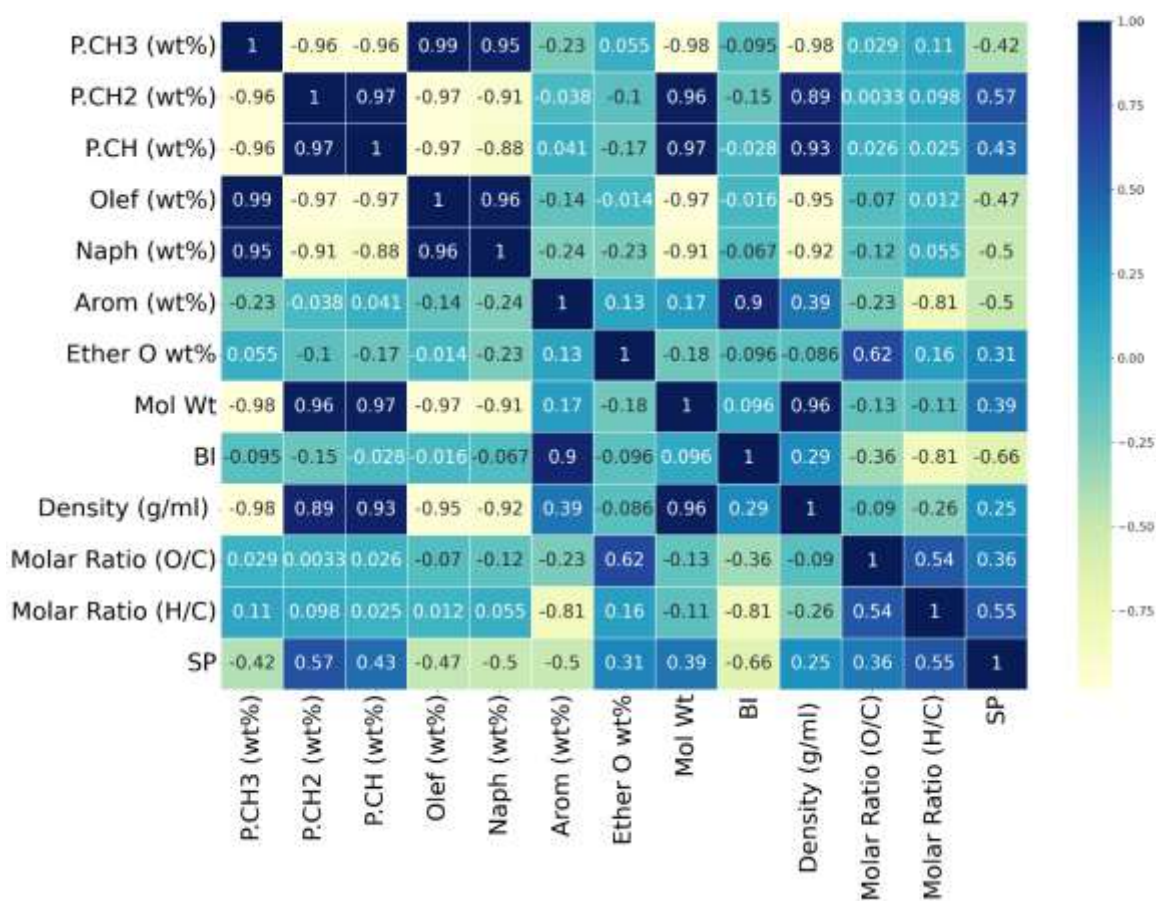


Figure 40: Input and output features represented using Pearson's correlation for SP model.

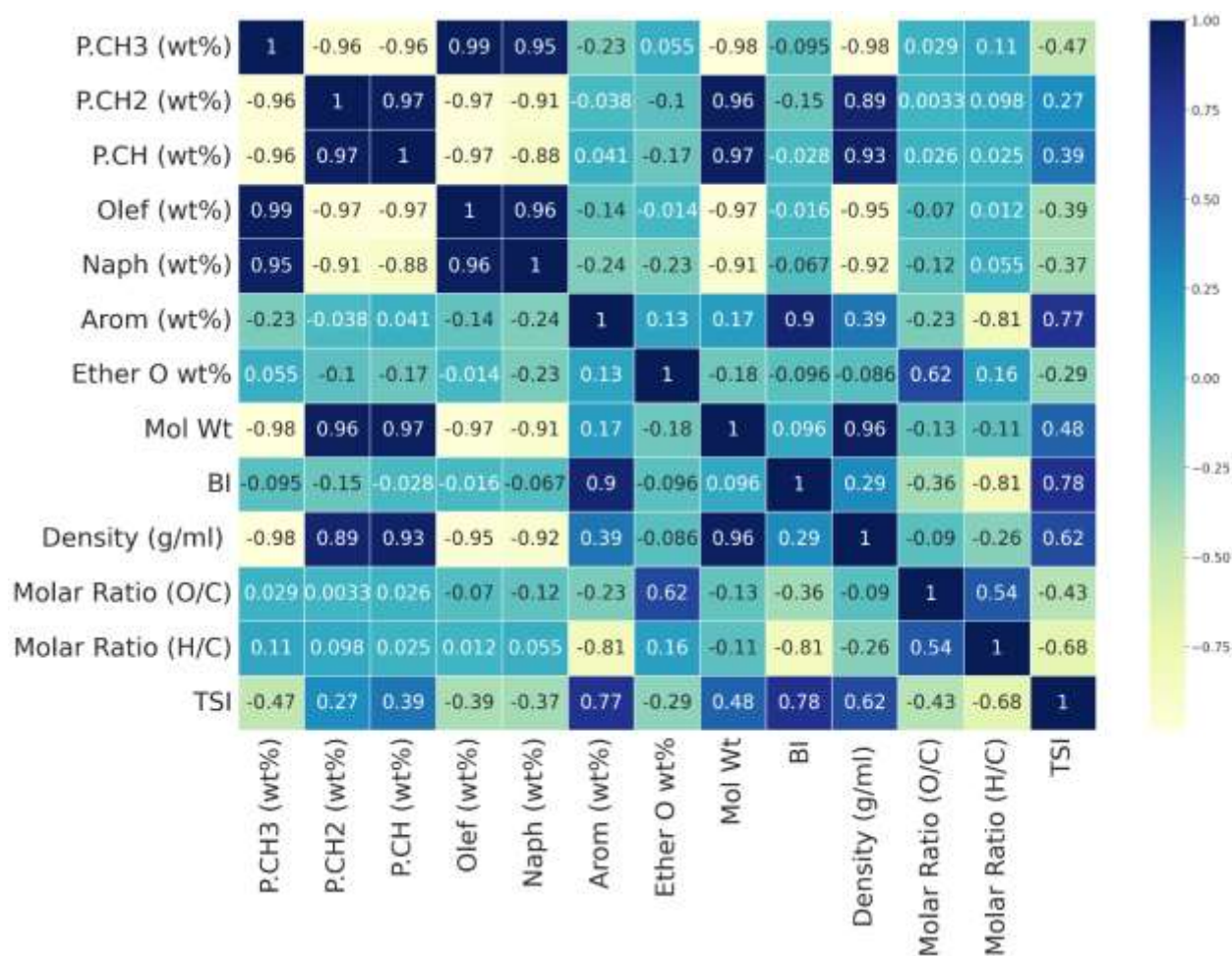


Figure 41: Input and output features represented using Pearson's correlation for TSI model.

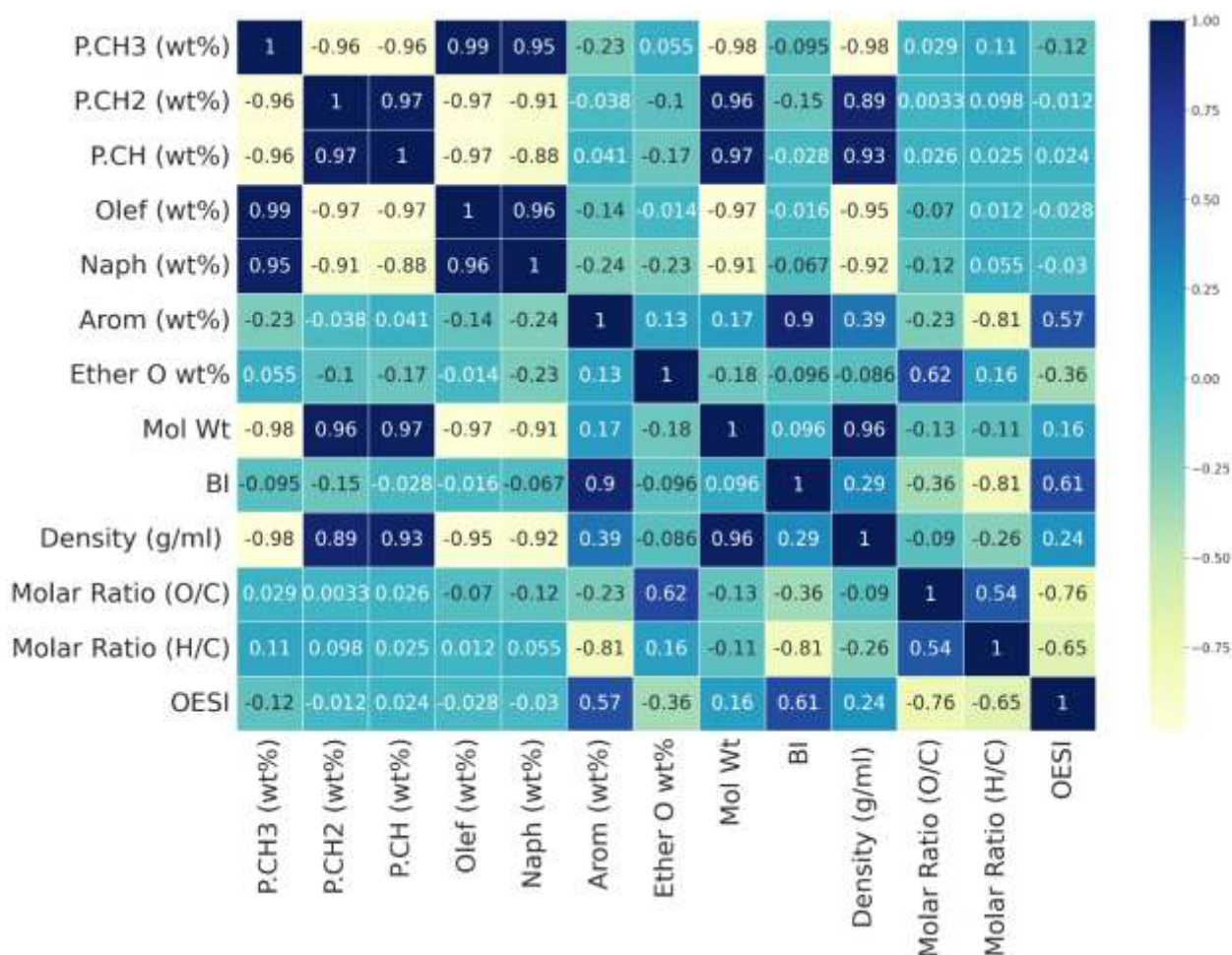


Figure 42: Input and output features represented using Pearson's correlation for OESI model

4.4.1.4 Model ANN

The SP, TSI, and OESI values were predicted using the final ANN models developed with 12 input features. Optimal hyperparameters (hidden layers, neurons, and epochs) for SP, TSI, and OESI models were determined through continuous optimization of neural network topology, as shown in Tables 12, 13 and 14, respectively. Finalized parameters included one hidden layer with 10 neurons for all models, with 10, 9, and 18 epochs for SP, TSI, and OESI, respectively. To assess prediction accuracy, the mean of the predicted SPs was calculated using the test set, which comprised 15% of the data

and was not used during training or fine-tuning. The test set, selected automatically via a MATLAB built-in function, served as a criterion for evaluating model performance. Measured and predicted SPs were plotted using the test set to assess model accuracy, with the same process applied for predicting TSI and OESI. This resulted in correlation factors (R) of 0.96, 0.99, and 0.98 for SP, TSI, and OESI, respectively, as shown in Figures 43, 44, and 45. Consequently, the developed models can accurately predict the SP, TSI, and OESI of petroleum fuels (diesel or gasoline) containing oxygenated additives using inputs such as functional groups, BI, density, and molar ratios of O/C and H/C.

The successful performance of these models is attributed to the use of advanced tools, including ANN. A key feature of this modeling technique—and the foundation of its predictive power—is that no two fuels in the dataset with identical SP, TSI, or OESI values share a similar distribution of functional groups. This highlights the model’s inherent capability to distinguish fuels based on the unique functional group composition of each blend, offering a valuable criterion for fuel quantification.

Table 12: Optimized hyperparameters of the final SP model

Parameter	description
Hidden layers	1
Neurons	10
Epochs	10

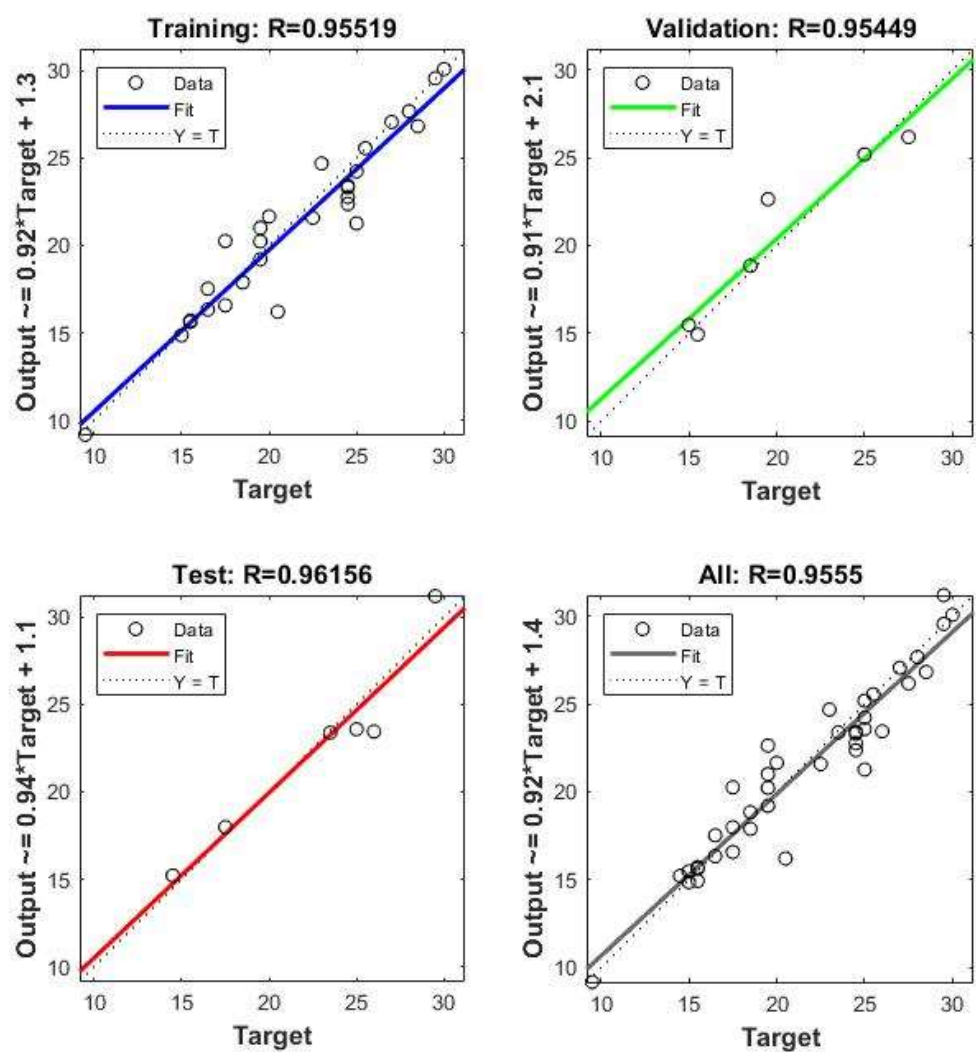


Figure 43: Comparison between the predicted and measured SPs.

Table 13: Optimized hyperparameters of the final TSI model

Parameter	description
Hidden layers	1
Neurons	10
Epochs	9

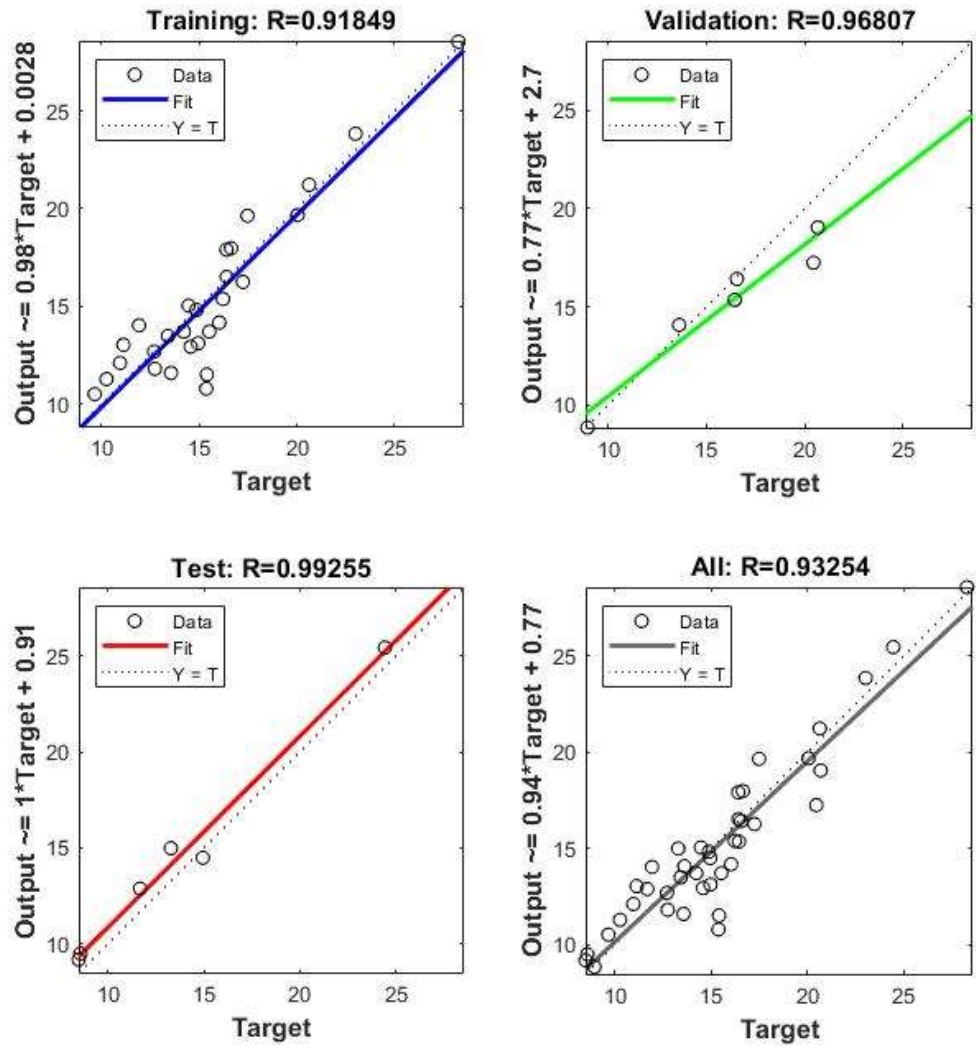


Figure 44: Comparison between the predicted and measured TSIs.

Table 14: Optimized hyperparameters of the final OESi model

Parameter	description
Hidden layers	1
Neurons	10
Epochs	18

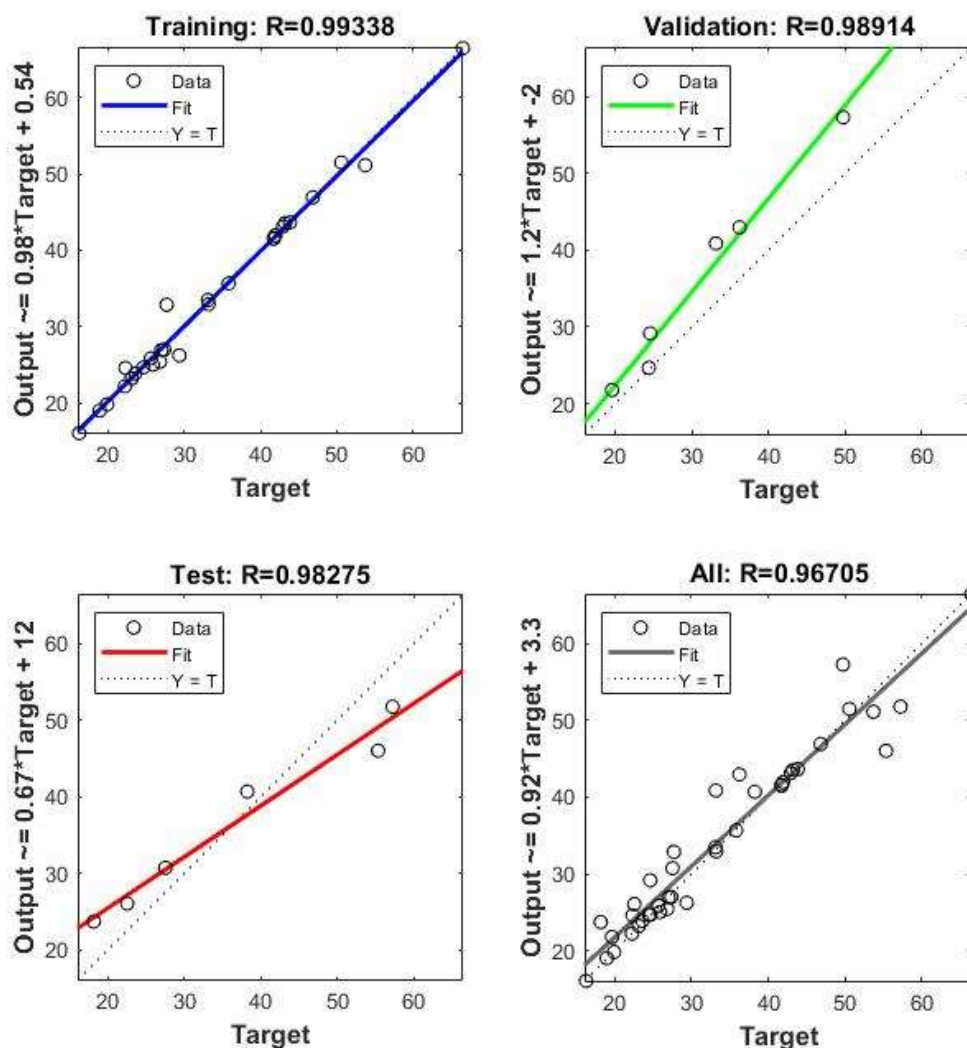


Figure 45: Comparison between the predicted and measured OESis.

4.5 Conclusion

The SP measurements, along with the TSI and OESI calculations, were used to analyze the sooting propensity of diesel/gasoline-oxygenated blends. Artificial neural network (ANN) tools were subsequently employed to develop AI models based on these SP measurements. The experiments involved 40-component blends with varying ether

percentages (1%, 5%, 10%, 20%) in diesel/gasoline-ether mixtures, incorporating ethers such as dibutyl ether, diethyl ether, diphenyl ether, dioctyl ether, and methyl tert-butyl ether (MTBE).

The inputs for the AI models included functional groups (CH₃, paraffinic CH₂, paraffinic CH, naphthenic CH-CH₂, olefinic -CH=CH₂, aromatic C-CH, and ether O groups), molecular mass (MM), branching index (BI), density, and molar ratios of O/C and H/C of the blends. The outputs were the indices (SP, TSI, or OESI). The predicted indices showed excellent correlations (R) with experimental values: 0.96 for SP, 0.99 for TSI, and 0.98 for OESI. The average errors for these indices were 1.16, 1.00, and 4.92, respectively

Chapter 5:

Characterization of soot emitted from the atmospheric combustion of diethyl ether-diesel blends.

Reducing emissions from the transportation sector due to their undesirable impact on environment [168-174] and human health [175] is one of the major challenges of the 21st century. Carbon emitted due to the use of fossil-fuel powered vehicles and other combustion sources has led to increased atmospheric CO₂ concentrations and is directly responsible for global warming. [176]. Although compression-ignition engines using diesel fuel emit less CO₂ compared to the gasoline powered spark-ignition engines due to their inherently better fuel efficiency, particulate matter (PM) and nitrogen oxide emissions are typically a major concern when using diesel engines.

Rigorous emission standards have been established around the world to reduce the harmful effects of engine-out emissions. In Europe, stringent limits for nitrogen oxides and PM emissions were set, with the requirement that all light-duty diesel powered vehicles meet the emission norms set in Euro 6 standard [177]. One of the strategies to reduce pollutant emissions is increasing the use of advanced low-carbon fuels and biofuels to partially replace fossil fuels. The use of biofuels for road transport has increased considerably in recent years, however, the recent introduction of the new RED-II sustainability and GHG emission criteria favors the use of advanced biofuels (such as ether or alcohols) [178] over traditional biofuels used earlier. Among the various ethers that can be blended with fossil diesel to reduce particulate emissions, diethyl ether has been selected here due to its advantageous properties (low flash point,

higher molar ratios of H/C and O/C, higher volatility, high cetane number, low viscosity, high heating value) [179].

In terms of transportation fuels, ethanol produced from renewable sources such as biomass is a promising fuel for spark-ignition engines due to its low reactivity and correspondingly high-octane number. However, it is not suitable for using as a fuel in compression-ignition engines due to the fundamentally different nature of the ignition process in the two aforementioned engines. Diethyl ether (DEE), on the other hand is very reactive and thereby has a high cetane number which makes it suitable as a fuel in compression-ignition engines. Moreover, DEE has a higher volumetric and gravimetric energy density compared to ethanol and can easily be produced from ethanol through a dehydrogenation process [179]. Although DEE has commonly been used for as a cold-start aid for compression-ignition engines, it has rarely been used as a fuel blend with diesel or as a pure fuel to replace diesel altogether.

Pollutant emissions can also be reduced to meet regulatory emission standards through the use of numerous emission-specific after-treatment processes. Nitrogen oxides emissions are typically reduced through the use of selective catalytic reduction (SCR) and lean nitrogen oxide traps (LNT) [180] in diesel engines. Diesel particulate filter (DPF) is generally used for trapping particulate emissions which are eliminated by regeneration process (oxidation process). There are various factors that influence the DPF performance including filter characteristics, exhaust gas composition, flow rate, flow profiles, temperature, as well as the physicochemical features of soot [181, 182]. Therefore, understanding the characteristics of soot to utilize appropriate oxidation

processes can potentially help in minimizing the adverse effects of the oxidation process on filter lifetime and fuel consumption[183].

Historically, various analysis techniques have been used to perform chemical, thermal, and nano-structural analysis of the soot characteristics. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) [184, 185], Raman spectroscopy [186, 187], and x-ray diffraction (XRD) [182, 188] were among the nano-structural techniques used. However, the results were inconsistent when researchers tried to relate the soot nano-structure to its oxidative reactivity. Interestingly, it has been found that decrease in fringe length and increased spacing between layers increases the oxidative potential of soot as more soot surface area is exposed due to weak van der Waals forces between the layers and the higher location of carbon atoms present at the edge site [189, 190]. Moreover, soot particle size has a great influence on soot oxidation as particle size possesses an inverse relationship with surface area of soot and accessibility of oxygen to carbon substrate [191]. Soot characteristics such as its ability to adsorb functional groups on the soot surfaces has been investigated using different analytical techniques including energy-dispersive X-ray spectroscopy (EDX)[192, 193], X-ray absorption fine structure (XAFS)[25,34], nuclear magnetic resonance (NMR) [194, 195], X-ray photoelectron spectroscopy (XPS) [196, 197] and infrared spectroscopy techniques [198, 199] including Fourier-transform infrared (FTIR), Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and attenuated total reflectance (ATR). Several studies have examined the relationship of aliphatic and oxygenated compounds with soot reactivity [181, 199, 200]. Lastly, thermal techniques such as thermal scanning of differential calorimetry (DSC) and gravimetric analysis have also

been used for assessing the soot reactivity. The soot reactivity is analyzed by tracking the temperature needed for oxidation under a heating ramp or by the time required for oxidation under an isothermal process.

Overall, it is important to note that conclusions on soot reactivity may be misleading or inconsistent if they are based solely on chemical and structural analysis. Therefore, in addition to chemical and structural analysis, the current study investigates the effect of micro/nano structure, morphology and functional groups on soot reactivity.

5.1 Experimental

5.1.1 Materials

A standard aluminum foil (silver color) was used to collect the soot in this study. A standard SP lamp purchased from Koehler, USA was used for establishing the atmospheric diffusion flame. n-Heptane (99.5%), diethyl ether with purity between 99 to 99.5%, and deuterated chloroform (Chloroform-d) (CDCl₃) "100" (min. 99.96 atom % D) were purchased from Sigma Aldrich. Diesel samples were obtained from the retail refueling stations in Dharan, Kingdom of Saudi Arabia.

5.1.2 Methodologies

All the experimental studies were performed according to ASTM D1322 standard as explained in detail [201]. The soot emitted from the candle flame of the SP lamp was collected for each fuel sample by covering the SP lamp with aluminum foil as shown in Figure 1.

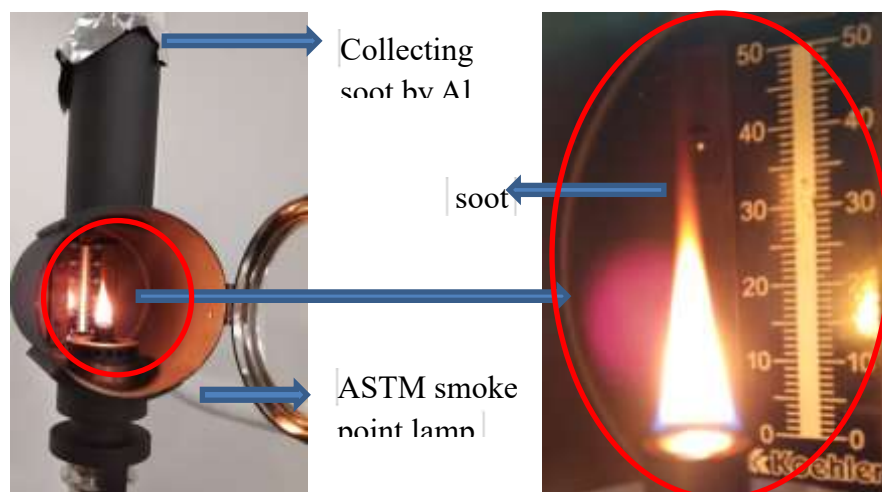


Figure 46: Collection of the soot using the Al foil covering the SP lamp.

Morphologies of diethyl ether /diesel samples were analyzed using SEM from Jeol (Model No. JSM6610LV). The composition of the soot product was determined by EDX Jeol. The features of the nanoparticles were analyzed by a TEM from Joel (Model No. JEM2100F). The soot reactivity/oxidation was determined using thermogravimetric analysis (TGA) instrument from national scientific company limited (Model No: SDT Q600). The TGA experiments were performed under a constant heating rate of $10^{\circ}\text{C}/\text{min}$ at a temperature range between 25°C to 1000°C and under two different atmospheres (air and nitrogen). Samples with initial weights of approximately 2-6 mg were kept in the furnace after determining the weight by calibration. The sample was then heated up to 1000°C with a 100 ml /min flow of nitrogen or air at a constant rate of heating of $10^{\circ}\text{C}/\text{min}$. The composition of elements C, H, N, and S generated from combustion products (CO_2 , H_2O , NO_2 , and others) was determined using a Vario MICRO cube CHNS analyzer from Elementar. The structure, phase, molecular interactions, and crystallinity of the samples were analyzed using a Raman spectrometer from Horiba (Model No. IHR-320). The chemical structure,

composition, and physical properties were determined by XRD. PXRD patterns were gained from the Rigaku X-ray diffractometer, with X-ray radiation from Cu $k\alpha$ ($\lambda = 1.541 \text{ \AA}$) source. Finally, the hydrogen atoms' positions in the molecules were identified using high resolution liquid state ^1H -NMR (Model No. AVANCE III 9.4 T) in a single-pulse experiment. Deuterated chloroform (CDCl_3) was used as a solvent for dissolving the soot obtained from diethyl ether-diesel (DEED) blends.

5.2 Results and discussion

Combustion of diesel/fuel blends lead to the formation of soot and other products through numerous thermal decomposition processes. The soot particles produced from this process appear individually and are extremely small thereby have the tendency to spread out in the surrounding air. However, some of the soot particles aggregate to form relatively larger sized agglomerates. These particles produced from the combustion of diesel with atmospheric air consist of elemental carbon, various hydrocarbons, compounds including sulfur like polyaromatic sulfur heterocycles (PASH), and a variety of other species [202-204]. Therefore, the aforementioned techniques were used for characterizing the two diesel fuel blends with diethyl ether to deeply investigate its impact on the soot formation. For all the results discussed in this work, the soot was obtained from a diffusion flame of diesel-diethyl ether blends produced in a SP lamp following the ASTM D1322 standard.

5.2.1 Scanning electron microscopy (SEM)

The SEM images in Figure 2 (a and b) represent the soot collected from a blend consisting of 5 % diethyl ether and 95 % diesel by volume (DEE5D) and Figure 2 (c and d) represent the soot from 20 % diethyl ether and 80 % diesel by volume (DEE20D)

blend. The surface morphology of the soot obtained is non-uniform with different grains of nanomaterial observed in the micrograph of 0.5 μm in Figures 2a and 2c. The soot particles are too small and the agglomerations of particles formed through the aggregation of irregular particles is also shown in Figures 2a and 2c. Therefore, from the above-mentioned SEM images, it is difficult to classify the observed soot nanoparticles as or nanospheres.

5.2.2 Low/high resolutions of transition electron microscopy (LR/HR-TEM)

The low-resolution TEM (LR-TEM) images of the soot obtained from the combustion of diesel-diethyl ether (DDEE) blends soot are presented in Figures 2b (DEE5D: 5%diethyl ether and 95% diesel v/v)) and 2d (DEE20D: 20%diethyl ether and 80% diesel v/v)). Spherules gathered in large concentrations to create fractal-like geometric structures. From the figures, one can observe some well-known diesel soot characteristics. First, the sizes of the total aggregates varied significantly. Second, the shapes of the particles varied and exhibited structures like grapes [205]. The spherule sizes were mostly constant. Additionally, the distinctions between the spherules were hazy. The typical soot macrostructures found in the DEE5D and DDE20D samples are shown in Figures 2b and 2d, respectively. While DEE20D soot is less clumped because of a higher percentage of diethyl ether, DEE5D soot has more intricate chains. While DDE5D soot is more densely packed, DEE20D chains are looser and more open-looped. The spherules' irregular, deformed shapes—indicative of young soot—are another characteristic that sets both soot's apart [206].

Nanomaterials (shown in LR-TEM images at 200 nm) obtained from the blend soot resemble nanospheres. These nanospheres are agglomerated in the high resolution TEM (HR-TEM) images of Figures 2b and 2d shown later in Figures 3a and 3b.

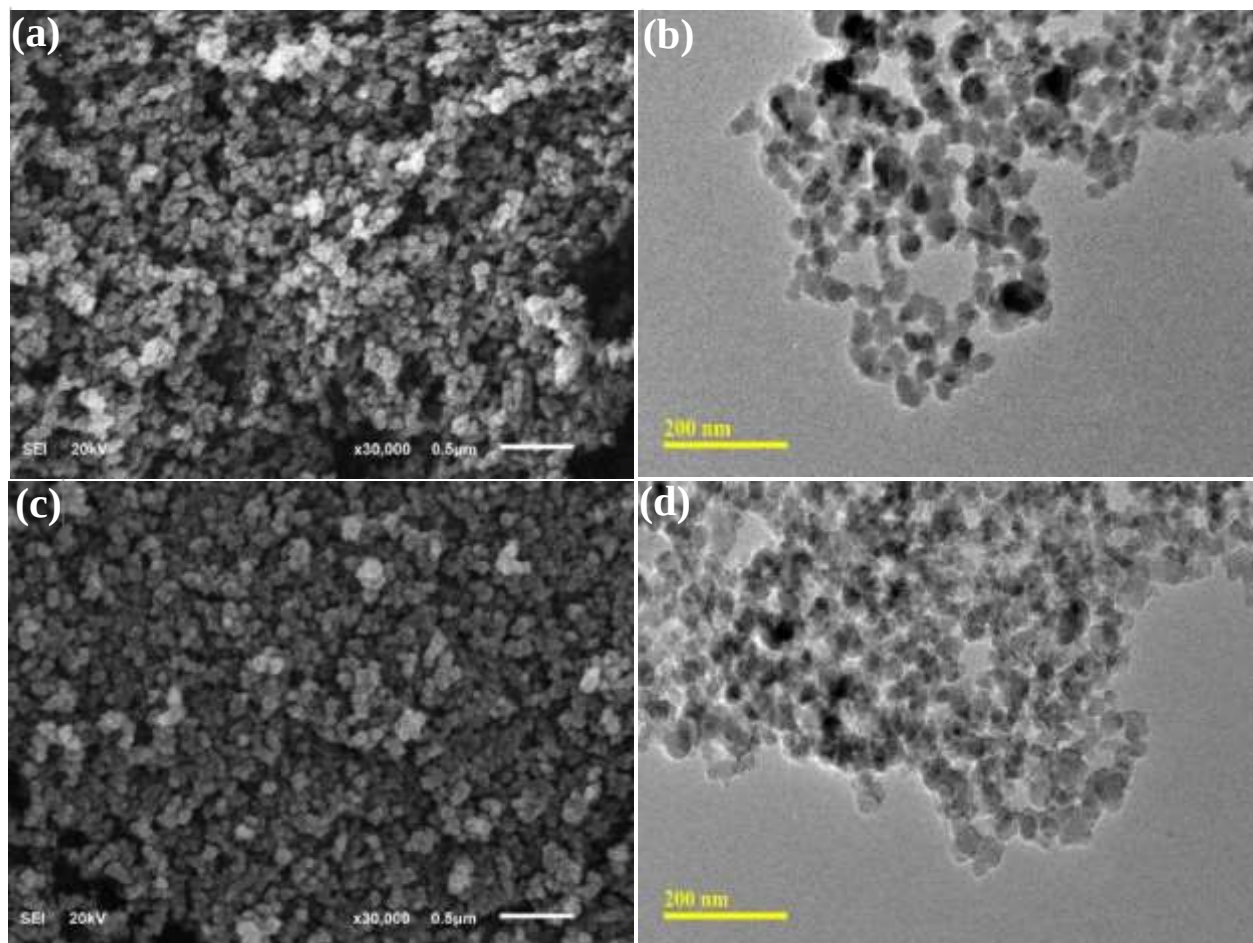


Figure 47: Soot from the atmospheric combustion of diesel-oxygenates blend:(a and b) 95 vol% diesel 5vol% diethyl ether (DEE5D) and (c and d) 80 vol% diesel 20 diethyl ether (DEE20D)

From Figures 3a (DEE5D) and 3b (DEE20D), the single nanocarbon indicate that nanospheres in general are uniform in shape. Moreover, the particle size for both blends

is similar with average diameters of DEE5D and DEE20D being 36 and 38 nm respectively as shown in HR-TEM images of Figures 3a and 3b.

Figures 3c (DEE5D) and 3d (DEE20D) illustrate the effect of increasing diethyl ether content on the interplanar distance of graphite layers. The circle in Figure 3d indicates that the crystalline structure/interplanar distance of soot obtained from the DEE20D blend is more ordered than that from DEE5D (the circle in Figure 3c). This trend can be attributed to the oxygen present in diethyl ether-diesel blends. Oxygen is known to attack the active centers located in the structures of defects which are more common in the shorter layers. Hence, these layers are more prone to oxidation and are likely to be destroyed/consumed due to their small size.

A soot with more occupied edge sites does have a higher reactivity because a carbon atom at an edge site is significantly more active than one in the lattice of a graphene layer. By reducing the size of the graphene layer within the particle, it is possible to boost this edge site population density [207-209]. The thickness of each graphitic layer was calculated from figures 3c and 3d to be 5/10 nm and 6/15 nm of the diameter of the circle divided by the number of layers for DEE5D and DEE20D soot respectively. This was calculated by dividing the thickness (the circle diameters measured by Image J software) of crystallites stacked together by the number of layers included in the circle. The circles were magnified and shown at the right-side corners of Figures 3c and 3d. The graphitic layer thickness still differs by 0.1 nm, despite the fact that this partly suggests that the increase in diethyl ether content has a minimal impact. It can be deduced from the findings presented here that the thickness (distance) reduction of the layers is caused by increased diethyl ether and, consequently, oxygen

concentration, even though the difference in the interplanar distance for different soot samples occasionally is not significant due to overlap among error bars. Also, the soot produced by the DEE20D blend has a more organized crystalline structure and interplanar distance than soot produced by the DEE5D blend.

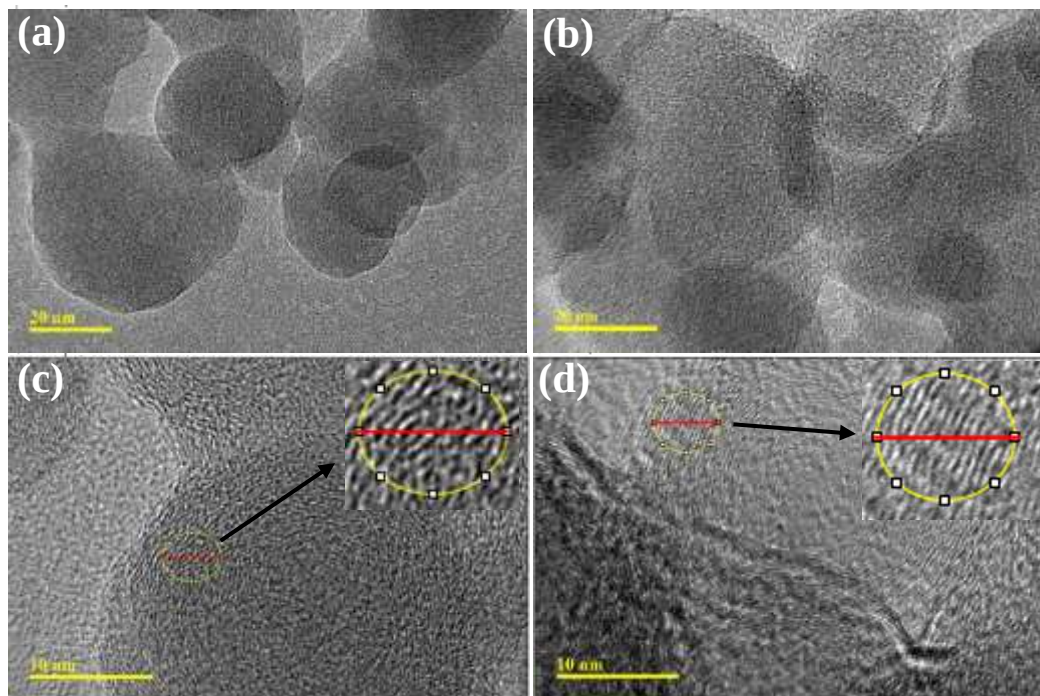


Figure 48: HR-TEM images of soot obtained from the atmospheric combustion of diesel-diethyl-ether blend:(a and c) 5% vol diethyl ether and 95 % vol diesel (DEE5D) and (b and d): 20% vol diethyl ether and 80 vol% diesel (DEE20D)

5.2.3 CHNS analyzer and Energy-dispersive X-ray spectroscopy (EDS/EDX)

Table 15: The combustion products from diethyl ether blend soot using a Vario MICRO cube CHNS analyzer.

The diethyl ether diesel blend soot	The Weight [mg]	N [wt%]	C [wt%]	H [wt%]	S [wt%]
DEE5D (5%Diethyl ether and 95% Diesel(v/v))	2.23	0.11	94.99	1.48	0.33
DEE20D(20%Diethyletherand 80% Diesel(v/v))	2.50	0.12	94.18	1.21	0.28

The CHNS analyzer shows that the soot from DEE5D and DEE5D blends consists of 0.11,94.99,1.48 and 0.33 wt% ; and 0.12,94.18,1.21 and 0.28 wt% for N, C, H, and S, respectively, as shown in Table 1. Although it was found that the DEE20D contained less sulfur (0.28%) than the DEE5D (0.33%) due to a lower percentage volume of diesel in the blend as shown in Figure 4a, this may also be because the DEE20D's higher oxygen concentration and lower aromatic content that increased the soot oxidation's reactivity. However, using EDS the composition of DEE5D consists of 80% C, 18.8%N,0.9% O, and 0.3% S, but DEE20D consists of 82.8% C,14.5% O, and 2.8% S. EDS spectra showing the composition of soot generated from DEE5D blend is presented in Figure 4b, but DEE20D soot is not shown here. Regarding the carbon percentage, the results from EDS are in good agreement with those from the CHNS analyzer, however there is considerable disagreement in the results for other elements. Due to the nature of CHNS measurements, the results are expected to be more accurate than EDS which relies on capturing a small specific area of the flame.

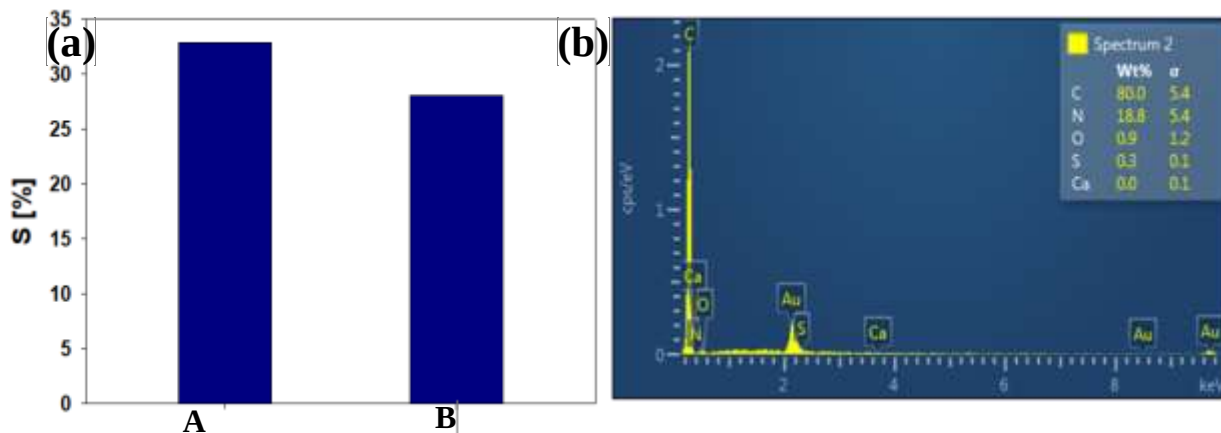


Figure 49: Soot from the atmospheric combustion of diesel-diethyl ether blend has : (a) Percentage of the sulfur of (A) DEE5D and (B) DEE20D using CHNS analyzer; and (b) Spectra of Energy dispersive spectroscopy (EDS) of DEE5D

5.2.4 X-ray diffraction (XRD)

The XRD results of the soot tested are shown in Figure 5a. The obtained peaks of Bragg diffraction appeared at $2\theta \approx 24^\circ$ and $2\theta \approx 43^\circ$. These two peaks indicate the presence of graphitic crystallite planes [210]. Where $2\theta \approx 24^\circ$ representing the plane of 002 is often asymmetric due to the superimposition of the Y band at lower values of 2θ on the left side of the figure 5a. These two peaks are corresponded to hexagonal lattice of graphite of multi-walled carbon nanotubes (MWCNT) [211, 212], but the nanoparticles are not looked MWCNT, in the SEM and TEM results. The high intensities of peaks at $2\theta \approx 24^\circ$ point out the presence of big amounts of amorphous material along with nanotubes. On the other hand, the low intensities of peaks at $2\theta \approx 43^\circ$ indicate that the soot has carbon nanomaterial with a low quality.

In the same Figure 5a, the two intensities of the peak of DEE5D soot decreased as the diethyl ether content increased from 5 to 20% in the fuel blend. Increasing the intensity of the peaks in XRD spectra indicates increasing the crystallinity and thus the size of

the particles and vice versa [10, 12, 13, 213, 214]. This can be explained by several parameters like crystallinity, diethyl ether content, particle sizes, aromatic content, and oxidation. When the diethyl ether content increases from 5% to 20% v/v in the diesel blend, the DEE20D soot is more amorphous (less crystallinity) than DEE5D one. This can be explained by increasing the soot reactivity where increasing the content of diethyl ether lead to increase the particle's disorder and amorphous characteristic which in turn enhances the edge site population density. A soot with numerous populated edge sites has a higher catalytic activity because a carbon atom at an edge site is substantially more energetic than one in the crystal lattice of a graphene layer [207-209]. Furthermore, when the diethyl ether content increases in the blend, the contents of oxygen and aromatics, proportionally increase and decrease, respectively. This leads to the equilibrium between oxidation and particle growth, resulting in stable particle sizes. As the oxygen concentration increase in diesel, the equilibrium is achieved at smaller particles. This is caused by either the bond of the oxygen and lower aromatic content inhibiting the growth of the particle or the oxygen content enhancing the soot oxidation, or both [215]. Regardless, since the smaller soot particles have a higher ratio of surface /volume, their reactivity is expected to increase. The XRD results supports that increasing diethyl ether in the diesel enhances the reactivity of the obtained soot. However, these results related to the sizes of particles are not very well correlated to

TEM and SEM results.

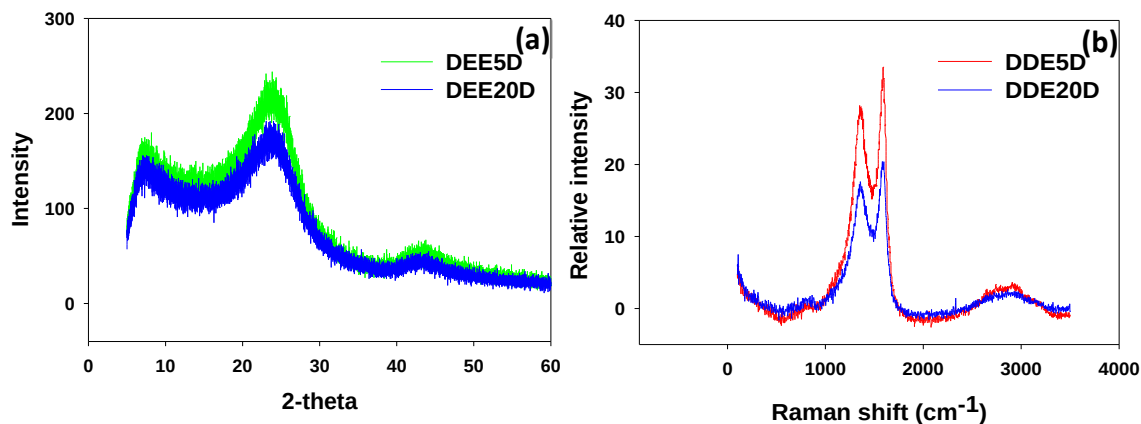


Figure 50: Raman (a) and X-ray diffraction (b) spectra of soot from the atmospheric combustion of diesel-diethyl ether blend (DEE5D: 5% Diethyl ether and 95% Diesel; and DEE20D: DEE5D: 20% Diethyl ether and 80% Diesel, v/v)

5.2.5 Raman spectroscopy

Raman spectroscopy was used to determine the degree of order in the internal structure of the soot produced from the combustion of diesel-diethyl ether blends (DEED) (Figure 5b). The spectra of DEE5D and DEE20D soot samples were similar, however they were distinguished from one another by the intensity of the peaks. Two major bands of D and G at approximately 1345 cm^{-1} and 1590 cm^{-1} respectively are shown in Figure 5a. The two bands are closer compared to literature values [182, 216], though the slight difference between them is likely due to the difference in the composition of fuel [182]. These two bands (D and G) are related to crystallites of graphitic carbon [182] or graphitic-like structures [217]. The D band (defect band) is associated with an amorphous carbon [216, 218, 219] and also indicates the presence of the graphitic chain

disorder due to crystalline defects, vacancies, and edges of graphene layers. Furthermore, the D band is attributed to stretched bonds of carbon-carbon in the net of crystalline such as those impurities of ions [220, 221]. And the G band (graphite band) is attributed to the soot microstructures order. Moreover, the G band corresponds to e_{2g} graphite mode, which is associated with the vibration of bonded carbon atoms of sp^2 [216]. The higher intensities bands represent DEE5D soot and the lower ones represent DEE20D one. Evaluating the soot nanostructure effects can be studied by calculating the peak intensities ratio of I_D/I_G bands (i.e., the intensity ratio (I_D/I_G) criterion has been chosen in this work despite the fact that there are other attributes for defining carbon structurally pertinent information on Raman). The structural defects present in the basal plane of the graphene layers are related to this ratio [182]. A higher ratio, a higher disorder in the nanostructure of soot. The two intensities ratios (I_D/I_G) of those two bands of DEE5D and DEE20D soot are ≈ 0.84 (lower disorder) and ≈ 0.89 (higher disorder), respectively. The DEE5D and DEE20D soot differ slightly from one another, indicating that the latter is more reactive than the former and that the soot reactivity is somewhat influenced by the soot structure and disorders. Therefore, as the diethyl ether content increases from 5 to 20% v/v in the fuel, the soot nanostructures become more disordered as shown in Figure 5b. The reason behind this could be due to the increasing oxidative reactivity of the soot by its nanostructures disorder which can be explained as follows. The oxygen content in the fuel; there is a relationship between initial oxygen content and structure where the oxygen concentration is not enough for removing the defects of the structure resulting in increased disorder of the soot nanostructures. Also, edge sites' surface oxygen groups have the ability to cause structural alterations when

attacked by air [222, 223]. A soot with more occupied edge sites does have a higher reactivity because a carbon atom at an edge site is significantly more active than one in the lattice of a graphene layer [207-209]. The graphene layer size can be reduced (as explained by TEM), the particle's disorder can be raised, and the primary particle can be made to have a more amorphous arrangement (as mentioned in the XRD) to improve the edge site population density. Most of these factors were achieved by increasing the content of diethyl ether in the diesel blend from 5% to 20% v/v. This finding is supportive of the idea that states that structure has an effect on the soot reactivity, which is consistent with [224] and inconsistent with those of [181, 187] associated with soot obtained from blends of biodiesel-diesel.

5.2.6 Proton nuclear magnetic resonance (^1H -NMR) spectroscopy

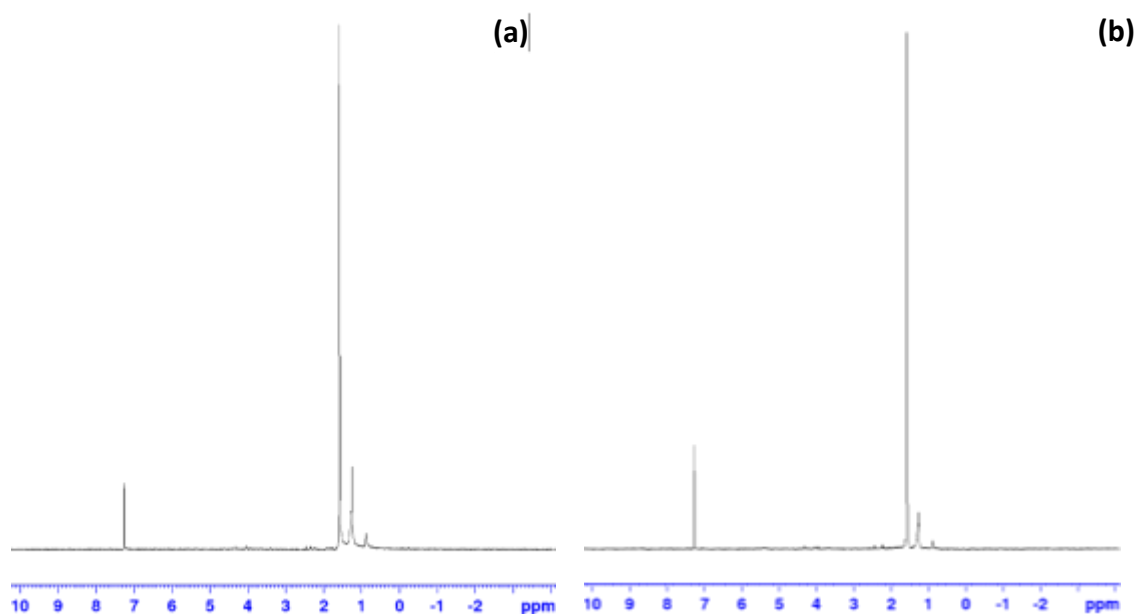


Figure 51: ^1H -NMR spectra of soot from the blend of (a) DEE5D (5% diethyl ether and 95 %diesel v/v) and (b) DEE20D (20% diethyl ether and 80 %diesel v/v) blends

¹H NMR is a common practice used for analyzing and characterizing heavy crude oils, gasoline, diesel, and coal fractions that are solvent-soluble. The structural data provided by the hydrogen groups identified by ¹H NMR spectra can be used to characterize complex mixtures made up of several paraffinic, isoparaffinic, aromatic, olefinic, and naphthenic compounds [225, 226]. Herein, ¹H NMR was used for characterizing the soot from combustion of diesel-ether blends. The various hydrogen atom types present in the soot produced from both diesel-diethyl ether blends (DEE5D (5 vol% diethyl ether and 95 vol% diesel) and DEE20D (20 vol% diethyl ether and 80 vol% diesel)) is shown in the two ¹H-NMR spectra as Figures 6a and 6b, respectively. The procedure suggested by Abdul Jameel et al. [79] was used to calculate the mole percentages of hydrocarbon functional groups [65, 227] from the ¹H NMR spectra. Bruker TopSpin 4.2 was the software used to calculate the integrated areas of the peaks. Table 2 displays the calculated mole percentages and chemical shift (ppm) regions of the groups.

According to Table 2 and Figures 6a and 6b, the major groups in both soots were, in general, the following: Naphthenic CH-CH₂ groups within 1.57 to 1.96 ppm; methyl (CH₃), methylene (CH₂), and CH groups connected to carbon atoms in position β of aromatic rings found between 1.0 and 2.0 ppm; hydrogen connected to aromatic rings found between 6.5 and 9 ppm; CH₃ hydrogen linked to carbon atoms γ and δ or to the higher-level position of aromatic rings; and CH₃ group of alkanes, cycloalkanes, and naphthenic rings located between 0.5 and 1.0 ppm [228]. There is a decrease in the paraffinic CH₃ groups in the soot when diethyl ether increases in the diesel blend from 5 to 20 vol%, as seen by the percentage moles of paraffinic CH₃ groups in DEE5D and

DEE20D soot, which are 8.03 and 2.63 %, respectively. Furthermore, as the diethyl ether concentration rose from 5 (DEE5D) to 20 (DEE20D) vol% in the diesel blend, the amount of paraffinic CH₂ groups in the soot increased from 27.51 to 19.38 mol%. However, the paraffinic CH groups increased from 17.05 to 35.25 mol% and showed the opposite trend. The concentration of the final two groups was noticeably reduced when the diethyl ether increased by 15% vol in the diethyl ether-diesel mix, as seen by the olefinic CH and CH₂ groups, whose total mole percentages are 0.45 and 0.01 in DEE5D and DEE20D soot, respectively. As the amount of diethyl ether grew from 5% to 20% (v/v) in the diesel blend, the total amount of naphthenic CH and CH₂ groups in the diethyl ether blend soot decreased from 42.36 to 37.46 mol%. Finally, there is no significant difference in the hydrogen-related aromatics in the DEE5D soot as the diethyl ether level in the diesel fuel (DEE5D) increased from 5 to 20 vol%.

As is commonly known, an increase in polycyclic aromatic hydrocarbons (PAHs) and soot precursors bound to the soot surface is expected to increase the concentration of surface aliphatic C-H groups. Meanwhile, a higher cylinder temperature and pressure can accelerate the carbonization reaction and dehydrogenation, which reduces the amount of aliphatic C-H groups [229, 230]. This explains why the functional groups of hydrogen change as the amount of diethyl ether in the diesel blend soot increases from 5 (DEE5D represented by part a in Figure 6) to 20 (DEE20D represented by part b in Figure 6) vol%. Additionally, as shown in Figure 7, the maximal loss of DEE20D soot begins at a slightly higher temperature than DEE5D, which accelerates the carbonization and dehydrogenation of aliphatic C-H groups. As a result, the percentages of the functional groups of paraffinic CH₃ and CH₂ decrease, but the CH

in the paraffinic chain increases as the diethyl ether content increases from 5 to 20% (v/v) in the diesel blend. The influence of diethyl ether, which may inhibit the production of naphthenic hydrocarbons by containing oxygen but no C=C bonds, leads to a decrease in the percentage of naphthenic CH-CH₂ groups, which may be the reason for better oxidation of DEE20D soot compared to DEE5D.

Both resultant soots contain a large number of naphthenic CH-CH₂ groups [231] and a significant number of aliphatic molecules, with a higher concentration of CH₂, CH, and aromatic ring positions β and γ [212, 228, 232]. Additionally, a sizable portion of hydrogen is linked to the Y position at about 0.8 ppm, indicating the presence of saturated rings or aliphatic chains linked to different kinds of aromatic rings. According to the results, when the volume percentage of diethyl ether reaches 20%, all hydrogen group concentrations from 0.25 to 6.42, except for paraffinic CH groups, which show an increase, decrease noticeably. This is followed by a small increase in the aromatic content between 6.42 and 8.99 ppm. Thus, there is a good correlation between the functional groups of hydrogen and the soot reactivity. Reactivity-wise, DEE20D soot is superior to DEE5D because the former has lower concentrations of paraffinic CH₃ and CH₂ groups, lower concentrations of naphthenic CH and CH₂ groups, and higher concentrations of paraffinic CH, all of which may be correlated with higher reactivity.

Table 16: ¹H-NMR functional groups and chimerical shift for DEE5D (5 vol% diethyl ether and 95 vol% diesel) and DEE20D (20 vol% diethyl ether and 80 vol% diesel) soot

chemical shift region (PPM)	H type	Mole percent (mol %)	
		DEE5D	DEE20D

0.25–0.94	paraffinic CH ₃ groups	8.03	2.63
0.94–1.39	paraffinic CH ₂ groups	27.51	19.38
1.39–1.57	paraffinic CH groups	17.05	35.25
4.50–6.42	olefinic CH and CH ₂ groups	0.45	0.02
1.57–1.96	naphthenic CH and CH ₂ groups	42.36	37.46
6.42–8.99	aromatics	4.60	5.26

5.2.7 Thermogravimetric (TGA) analysis

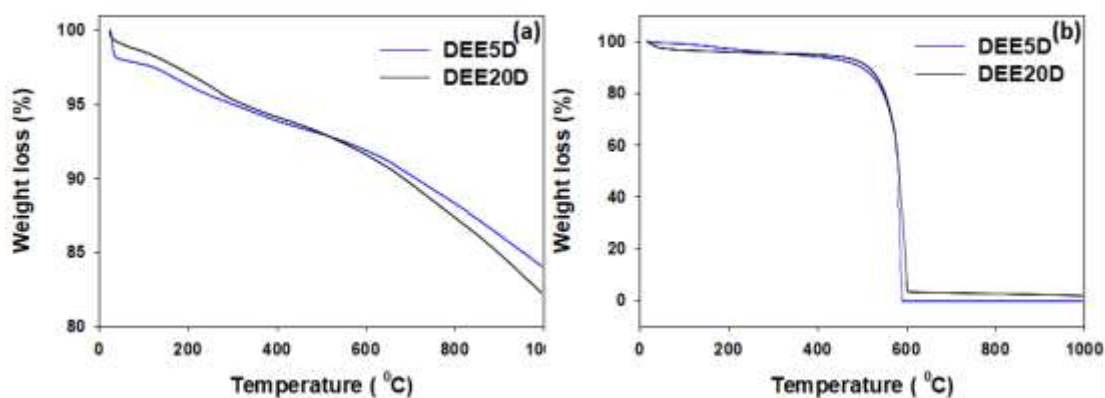


Figure 52: TGA curves of soot from Diethyl ether -Diesel blend (DEE5D: 5% Diethyl ether and 95% Diesel; and DEE20D: DEE5D: 20% Diethyl ether and 80% Diesel, v/v) (a) under N₂ atmosphere and (b) air

TGA was used to examine the oxidative reactivity of the soot generated from the two-diethyl ether-diesel blends (DEED). The temperature at which oxidation starts is an indicator of the thermal stability of soot, so it is used to determine the starting oxidation temperature. The temperature at which 5% of the initial mass of the soot is

lost is referred to as the starting temperature of the oxidation, and the temperature at which the mass loss rate becomes maximum is referred to as $MLRT_{max}$. Similarly, the temperature at which maximum heat release rate is achieved is indicated as $HRRT_{max}$. These temperatures are used as indicators of soot reactivity; the higher the values, the lower the oxidation related to soot reactivity[121, 233, 234] .

The composition of materials like lubricating oils, which mostly contains carbon as defined by ASTM 5967-08, is divided into four sections (A (<200 °C under an inert gas), B (200-700 °C under an inert gas), C (under an oxidative gas), and D (under an oxidative gas)) as analyzed by TGA [235]. The evaporated materials in two areas of A and B are high and medium components, respectively. Section C represents nonvolatile materials but those presented as unoxidized form can be oxidized. Those materials are called soot. Section D is soot material, which can't be volatilized or oxidized under conditions of sections A, B, and C named ash. Due to the different levels of thermal stability among their components, the aforementioned materials were split into four groups.

The TGA of the soot obtained from the diethyl ether-diesel blends under nitrogen and air is shown in Figures 7a and 7b, respectively. The TGA curve of the soot under nitrogen atmosphere shows a gradual weight loss from 100% to around 85% and 83 % for DEE5D and DEE20D, respectively during the temperature range of 25-1000°C. The weight loss represents the materials with high and medium volatilities. The removal of volatile organic fractions (VOF) during the devolatilization process causes the mass to decrease by about 5% at ≈ 400 °C. Although they each lost between 15 and 17% of their starting weight, there was no endothermic weight loss for either of them,

indicating that no products of the decomposition process were present. In other words, the pyrolysis process under N_2 produced no products since there was no thermal stability, as seen in Figure 7a. These findings are consistent with the study of [235]. Regarding the oxidation of the soot activity under N_2 , even if the oxidation temperatures for DEE5D and DEE20D soot are almost the same at 5% weight loss, the overall percentage of soot weight loss from DEE20D was a little bit greater than that from DEE5D during the range of 25–1000°C as shown in figure 7a. This might result from a rise in the diethyl ether content.

Regarding the TGA curves of soot under air, mass loss before about 550 °C resembles the materials evaporated under nitrogen, as previously mentioned. However, after this, sharp oxidation takes place, which results in the majority of mass being lost, with the exception of a very small amount, and denotes the thermal stability. However as seen in Figure 7b, raising the temperature considerably higher than 600 °C doesn't have the same effect on the residual material and indicates the presence of ash [235]. The temperature at which the oxidation process began for the soot produced by DEE20D was slightly lower than that of the soot produced by DEE5D, as shown in Figure 7b, even though the temperature at which the greatest mass loss occurred was roughly the same for both DEE5D and DEE20D. This shows that DEE20D has better soot reactivity (oxidation) than DEE5D. This might be because the diesel blend has more diethyl ether than usual. As consequence, this leads to an increase in the oxygen content as explained in the above sections. Thus, the kinetic rates of oxidation of the DEE20D soot with high oxygen content are much higher than those of DEE5D soot with low oxygen content. These results agree with those of biodiesel soot [181, 182, 196, 236,

237]. Furthermore, the increased reactivity of DEE20D soot samples may be attributed to the presence of more aliphatic and oxygenated functional groups. Another potential factor is the presence of more active surface regions that promote chemical reactions [26]. For DEE20D, devolatilization also results in a larger loss of soot mass. Soot particle-specific regions may increase during VOF desorption, according to various findings [13]. Soot oxidation may be further aided by the increased surface area caused by the removal of VOF. Although speculative, it is conceivable that DEE20D soot, like biodiesel soot [9], produces capsule-type oxidization (which burns faster than surface burning).

However, following maximum oxidation, it was noticeable that the residual weight of soot from DEE20D was slightly higher than that from DEE5D. Impurities or trace metals could be the cause of this variation. The remaining weight is primarily made up of accumulated ash, which represents a significantly higher amount of PM, because the DEE20D may have decreased emissions (e.g., sulphur), as indicated by CHNS data (particulate matter) [182]. This material (ash) is not volatile and not oxidizable as also observed in other studies [50]. Additionally, as was already noted, the temperature of $\approx 600^{\circ}\text{C}$ (where the most mass is lost) denotes the start of the blended soot's thermal stability, which leads to the development of carbonaceous soot or nanocarbon material.

5.3 Conclusion

It was determined that when the amount of diethyl ether in the diesel blend increases, the soot nanostructure disorder increases as demonstrated by XRD (lower peak intensities) and Raman spectroscopy (higher ID/IG ratio). The results of the Raman spectroscopy are somewhat in agreement with those from HR-TEM. The soot

nanostructure is more likely to disorganize when the diesel blend contains 20% v/v diethyl ether (higher (ID/IG:0.89)). As a result, the soot made from diethyl ether blends (DEE20D) should have a little higher reactivity than soot produced from DEE5D. This is comparable to the findings of the thermal analysis, which showed that DEE20D had a higher oxidation rate and soot reactivity than DEE5D. This suggests that the soot nanostructure has some influence on the reactivity of the soot in the diethyl ether-diesel blend. There is a high agreement between the data obtained from the CHNS analysis, XRD, Raman spectroscopy, ^1H -NMR, and the soot reactivity from the TGA analysis. The results from SEM, TEM, XRD, ^1H -NMR, and Raman spectroscopy showed some consistency with those results linked to soot reactivity. The sensitivity analysis revealed that the O/C ratio was the main factor influencing soot reactivity, with the nanostructure of the particles and the influence of aliphatic C-H functional groups having a medium effect. Furthermore, particle nanostructure, particularly the fringe tortuosity, had a little impact on soot reactivity.

Chapter 6: Conclusions and recommendations

The thesis involved measuring the smoke point using a smoke point lamp and developing ANN models using experimental datasets to predict the sooting tendency indices, namely SP, TSI, and OESi, of oxygenated fuels including various hydrocarbons (e.g., paraffins, naphthenes, olefins, aromatics), biomass-derived fuels (e.g., alcohols, and ethers), and mixtures (e.g., ethers + diesel or gasoline). Additionally, the work included the characterization of oxygenated fuels (ethers) blended with gasoline or diesel using sophisticated instruments such as a CHNS analyzer, EDS, SEM, TEM, XRD, TGA, Raman spectrometry, and ^1H -NMR.

The approach of functional groups was employed for predicting the sooting tendency of oxygenated fuels using ANNs. The SP model, trained on 366 fuel samples, demonstrated a strong correlation ($R^2 = 0.98$) with experimental values, with a mean absolute error of 4.5. Similarly, the TSI model, trained on 342 fuels, exhibited a regression coefficient ($R^2 = 0.97$) with an average absolute error of 2.46. Additionally, the model for OESi displayed an excellent correlation ($R^2 = 0.96$) with an average error of 4.92.

The study also tested the influence of soot particle nanostructure on reactivity, particularly in diesel/gasoline-oxygenated blends. Results showed the importance of the O/C ratio and aliphatic C-H functional groups on soot reactivity, with nanostructure impacting reactivity to a lesser extent.

Recommendations include utilizing advanced instruments for precise measurements, exploring biomass blends to reduce emissions, and employing various AI tools for predictive modeling like Convolutional Neural Networks (CNNs) instead of ANNs.

Future research aims to develop low-sooting fuels using predictive models and optimize oxygenated fuels as additives for specific combustion applications.

|

References

- [1] R. Sims, V. Goresvski, and S. Anenberg, "Black carbon mitigation and the role of the global environment facility: A STAP advisory document," 2015.
- [2] T. C. Bond *et al.*, "Bounding the role of black carbon in the climate system: A scientific assessment," *Journal of geophysical research: Atmospheres*, vol. 118, no. 11, pp. 5380-5552, 2013.
- [3] W. H. Organization, "Reducing global health risks through mitigation of short-lived climate pollutants. Scoping report for policy-makers," 2015.
- [4] N. A. Janssen *et al.*, *Health effects of black carbon*. World Health Organization. Regional Office for Europe, 2012.
- [5] J. S. Gaffney, N. A. Marley, and J. E. Frederick, "Formation and effects of smog," *Environmental and Ecological Chemistry; Sabljic, A., Ed.; Eolss Publishers Co., Ltd.: Oxford, UK*, vol. 2, pp. 25-51, 2009.
- [6] E. Oksanen and S. Kontunen-Soppela, "Plants have different strategies to defend against air pollutants," *Current Opinion in Environmental Science & Health*, vol. 19, p. 100222, 2021.
- [7] K. Arole *et al.*, "Impacts of particles released from vehicles on environment and health," *Tribology International*, p. 108417, 2023.
- [8] M. Karvonen, R. Kapoor, A. Uusitalo, and V. Ojanen, "Technology competition in the internal combustion engine waste heat recovery: a patent landscape analysis," *Journal of Cleaner Production*, vol. 112, pp. 3735-3743, 2016.
- [9] X. Liu *et al.*, "Computational study of hydrogen engine combustion strategies: Dual-Fuel compression ignition with Port-and Direct-Injection, Pre-Chamber Combustion, and Spark-Ignition," *Fuel*, vol. 350, p. 128801, 2023.
- [10] M. A. A. Qasem, A. Khan, S. A. Onaizi, H. D. Mohamed, A. Helal, and M. J. J. o. A. E. Aziz, "Effect of Co (NO₃) 2· 6H₂O thermal decomposition temperature on the nano-Co₃O₄ product morphology and electrocatalysis of water oxidation," vol. 49, no. 3, pp. 251-259, 2019.
- [11] M. A. A. Qasem, M. A. Aziz, M. Qamaruddin, J. P. Kim, and S. A. Onaizi, "Influence of pamoic acid as a complexing agent in the thermal preparation of NiO nanoparticles: application to electrochemical water oxidation," *ChemistrySelect*, vol. 3, no. 2, pp. 573-580, 2018.
- [12] M. A. Aziz and M. A. A. Qasem, "Method of making Co₃O₄ nanorods for electrocatalytic water splitting," ed: Google Patents, 2020.
- [13] M. A. Aziz and M. A. A. Qasem, "METHOD OF MAKING NiO NANOPARTICLES FOR ELECTROCATALYTIC WATER SPLITTING," ed: Google Patents, 2019.
- [14] M. A. Ahmed Qasem, M. Aziz, A. S. Hakeem, and S. A. Onaizi, "Preparation of nano-Co₃O₄ by direct thermal decomposition of cobalt (II) nitrate hexahydrate for electrochemical water oxidation," *Current Nanoscience*, vol. 14, no. 2, pp. 154-159, 2018.
- [15] A. G. A. Jameel *et al.*, "A minimalist functional group (MFG) approach for surrogate fuel formulation," *Combustion and Flame*, vol. 192, pp. 250-271, 2018.

- [16] A. G. Abdul Jameel, V. Van Oudenhoven, A.-H. Emwas, and S. M. Sarathy, "Predicting octane number using nuclear magnetic resonance spectroscopy and artificial neural networks," *Energy & fuels*, vol. 32, no. 5, pp. 6309-6329, 2018.
- [17] A. Abdul Jameel and S. Sarathy, "Prediction of RON and MON of gasoline-ethanol using ^1H NMR spectroscopy," *Proc. Eur. Combust. Meet*, 2017.
- [18] P. Geng and D. Conran, "Correlation of Chemical Compositions and Fuel Properties with Fuel Octane Rating of Gasoline Containing Ethanol," SAE Technical Paper, 0148-7191, 2011.
- [19] A. Lapidus, E. Smolenskii, V. Bavykin, T. Myshenkova, and L. Kondrat'ev, "Models for the calculation and prediction of the octane and cetane numbers of individual hydrocarbons," *Petroleum Chemistry*, vol. 48, no. 4, pp. 277-286, 2008.
- [20] A. G. Abdul Jameel, A. M. Elbaz, A.-H. Emwas, W. L. Roberts, and S. M. Sarathy, "Calculation of average molecular parameters, functional groups, and a surrogate molecule for heavy fuel oils using ^1H and ^{13}C nuclear magnetic resonance spectroscopy," *Energy & Fuels*, vol. 30, no. 5, pp. 3894-3905, 2016.
- [21] H. Yuan, B. Yang, and J. Yang, "Predicting properties of biodiesel fuels using mixture topological index," *Journal of the American Oil Chemists' Society*, vol. 86, no. 4, pp. 375-382, 2009.
- [22] T. Le Thuy and D. T. Allen, "Property estimation using structural characterizations: heat capacities of coal liquids," *Fuel*, vol. 64, no. 12, pp. 1754-1759, 1985.
- [23] S. Benson *et al.*, "Chem. Rev," *Chem. Rev.*, vol. 69, p. 279, 1969.
- [24] D. A. Saldana *et al.*, "Flash point and cetane number predictions for fuel compounds using quantitative structure property relationship (QSPR) methods," *Energy & Fuels*, vol. 25, no. 9, pp. 3900-3908, 2011.
- [25] B. Creton, C. Dartiguelongue, T. de Bruin, and H. Toulhoat, "Prediction of the cetane number of diesel compounds using the quantitative structure property relationship," *Energy & Fuels*, vol. 24, no. 10, pp. 5396-5403, 2010.
- [26] J. Hernández-Trujillo and R. F. Bader, "Properties of atoms in molecules: atoms forming molecules," *The Journal of Physical Chemistry A*, vol. 104, no. 8, pp. 1779-1794, 2000.
- [27] R. Sumathi, H.-H. Carstensen, and W. H. Green, "Reaction rate prediction via group additivity part 1: H abstraction from alkanes by H and CH_3 ," *The Journal of Physical Chemistry A*, vol. 105, no. 28, pp. 6910-6925, 2001.
- [28] R. Sumathi, H.-H. Carstensen, and W. H. Green, "Reaction rate prediction via group additivity, part 2: H-abstraction from alkenes, alkynes, alcohols, aldehydes, and acids by H atoms," *The Journal of Physical Chemistry A*, vol. 105, no. 39, pp. 8969-8984, 2001.
- [29] R. Sumathi, H.-H. Carstensen, and W. H. Green, "Reaction rate predictions via group additivity. Part 3: Effect of substituents with CH_2 as the mediator," *The Journal of Physical Chemistry A*, vol. 106, no. 22, pp. 5474-5489, 2002.
- [30] P. Pepiot-Desjardins, H. Pitsch, R. Malhotra, S. Kirby, and A. L. Boehman, "Structural group analysis for soot reduction tendency of oxygenated fuels," *Combustion and Flame*, vol. 154, no. 1-2, pp. 191-205, 2008.

- [31] Y. Yang, A. L. Boehman, and R. J. Santoro, "A study of jet fuel sooting tendency using the threshold sooting index (TSI) model," *Combustion and Flame*, vol. 149, no. 1-2, pp. 191-205, 2007.
- [32] S. Yan, E. G. Eddings, A. B. Palotas, R. J. Pugmire, and A. F. Sarofim, "Prediction of sooting tendency for hydrocarbon liquids in diffusion flames," *Energy & fuels*, vol. 19, no. 6, pp. 2408-2415, 2005.
- [33] E. J. Barrientos, M. Lapuerta, and A. L. Boehman, "Group additivity in soot formation for the example of C-5 oxygenated hydrocarbon fuels," *Combustion and Flame*, vol. 160, no. 8, pp. 1484-1498, 2013.
- [34] S. Dooley *et al.*, "A jet fuel surrogate formulated by real fuel properties," *Combustion and flame*, vol. 157, no. 12, pp. 2333-2339, 2010.
- [35] S. H. Won, S. Dooley, F. L. Dryer, and Y. Ju, "A radical index for the determination of the chemical kinetic contribution to diffusion flame extinction of large hydrocarbon fuels," *Combustion and Flame*, vol. 159, no. 2, pp. 541-551, 2012.
- [36] S. Dooley *et al.*, "The experimental evaluation of a methodology for surrogate fuel formulation to emulate gas phase combustion kinetic phenomena," *Combustion and Flame*, vol. 159, no. 4, pp. 1444-1466, 2012.
- [37] F. M. Haas, A. Qin, and F. L. Dryer, "'Virtual' Smoke Point Determination of Alternative Aviation Kerosenes by Threshold Sooting Index (TSI) Methods," in *50th AIAA/ASME/SAE/ASEE Joint Propulsion Conference*, 2014, p. 3468.
- [38] J. B. Heywood, *Internal combustion engine fundamentals*. McGraw-Hill Education, 2018.
- [39] A. Überall, R. Otte, P. Eilts, and J. Krahel, "A literature research about particle emissions from engines with direct gasoline injection and the potential to reduce these emissions," *Fuel*, vol. 147, pp. 203-207, 2015.
- [40] "Emission standards. EU: Cars and Light Trucks." <https://dieselnet.com/standards/eu/ld.php> (accessed.
- [41] "Emission standards. United States: Cars and Light-Duty Trucks: Tier 3." https://dieselnet.com/standards/us/ld_t3.php (accessed.
- [42] O. Armas, M. A. n. Gómez, E. J. Barrientos, and A. L. Boehman, "Estimation of opacity tendency of ethanol–and biodiesel–diesel blends by means of the smoke point technique," *Energy & fuels*, vol. 25, no. 7, pp. 3283-3288, 2011.
- [43] E. J. Barrientos, J. E. Anderson, M. M. Maricq, and A. L. Boehman, "Particulate matter indices using fuel smoke point for vehicle emissions with gasoline, ethanol blends, and butanol blends," *Combustion and Flame*, vol. 167, pp. 308-319, 2016.
- [44] A. Gómez, J. Soriano, and O. Armas, "Evaluation of sooting tendency of different oxygenated and paraffinic fuels blended with diesel fuel," *Fuel*, vol. 184, pp. 536-543, 2016.
- [45] H. Calcote and D. Manos, "Effect of molecular structure on incipient soot formation," *Combustion and Flame*, vol. 49, no. 1-3, pp. 289-304, 1983.
- [46] Mckinsey. "Energy Insights. Smoke Point " <https://www.mckinseyenergyinsights.com/resources/refinery-reference-desk/smoke-point/> (accessed.
- [47] A. W. Drews, *Manual on hydrocarbon analysis*. ASTM International, 1992.

- [48] (2012) ANNUAL STATEMENT OF RESERVES 2011– DNO INTERNATIONAL ASA Available: <https://www.dno.no/media/gegnqikm/dno-annual-statement-of-reserves-2011.pdf>
- [49] Y. Al-Beatiy, "Standard Test for Smoke Point for Kerosene and Aviation Turbine fuel, ASTM 1322-97, IP 57/95," 2014. [Online]. Available: <https://www.slideshare.net/yoyoalbeatiy/experiment-no9-smoke-point>
- [50] S. Parkash, *Refining processes handbook*. Elsevier, 2003.
- [51] T. Kessler, E. R. Sacia, A. T. Bell, and J. H. Mack, "Artificial neural network based predictions of cetane number for furanic biofuel additives," *Fuel*, vol. 206, pp. 171-179, 2017.
- [52] J. Herreros, A. Jones, E. Sukjit, and A. Tsolakis, "Blending lignin-derived oxygenate in enhanced multi-component diesel fuel for improved emissions," *Applied energy*, vol. 116, pp. 58-65, 2014.
- [53] R. Vallinayagam *et al.*, "Investigation of evaporation and engine characteristics of pine oil biofuel fumigated in the inlet manifold of a diesel engine," *Applied energy*, vol. 115, pp. 514-524, 2014.
- [54] S. S. Khalafalla, U. Zahid, A. G. Abdul Jameel, U. Ahmed, F. S. Alenazey, and C.-J. Lee, "Conceptual design development of coal-to-methanol process with carbon capture and utilization," *Energies*, vol. 13, no. 23, p. 6421, 2020.
- [55] B. Li, Y. Li, H. Liu, F. Liu, Z. Wang, and J. Wang, "Combustion and emission characteristics of diesel engine fueled with biodiesel/PODE blends," *Applied Energy*, vol. 206, pp. 425-431, 2017.
- [56] H. Liu, Z. Wang, J. Zhang, J. Wang, and S. Shuai, "Study on combustion and emission characteristics of Polyoxymethylene Dimethyl Ethers/diesel blends in light-duty and heavy-duty diesel engines," *Applied Energy*, vol. 185, pp. 1393-1402, 2017.
- [57] J. Liu, P. Sun, H. Huang, J. Meng, and X. Yao, "Experimental investigation on performance, combustion and emission characteristics of a common-rail diesel engine fueled with polyoxymethylene dimethyl ethers-diesel blends," *Applied Energy*, vol. 202, pp. 527-536, 2017.
- [58] A. Jameel and A. Gani, "Predicting Sooting Propensity of Oxygenated Fuels Using Artificial Neural Networks," *Processes*, vol. 9, no. 6, p. 1070, 2021.
- [59] O. I. Awad *et al.*, "Alcohol and ether as alternative fuels in spark ignition engine: A review," *Renewable and Sustainable Energy Reviews*, vol. 82, pp. 2586-2605, 2018.
- [60] A. D, "Standard test method for smoke point of kerosene and aviation turbine fuel," *Annual Book of Standards*, 2008.
- [61] Z. Gao, X. Zou, Z. Huang, and L. Zhu, "Predicting sooting tendencies of oxygenated hydrocarbon fuels with machine learning algorithms," *Fuel*, vol. 242, pp. 438-446, 2019.
- [62] M. Lapuerta, J. J. Hernández, and S. M. Sarathy, "Effects of methyl substitution on the auto-ignition of C16 alkanes," *Combustion and Flame*, vol. 164, pp. 259-269, 2016.
- [63] N. Naser, A. G. A. Jameel, A.-H. Emwas, E. Singh, S. H. Chung, and S. M. Sarathy, "The influence of chemical composition on ignition delay times of gasoline fractions," *Combustion and Flame*, vol. 209, pp. 418-429, 2019.

- [64] A. G. Abdul Jameel, "A functional group approach for predicting fuel properties," 2019.
- [65] B. D. Ilieş *et al.*, "Probing the chemical kinetics of minimalist functional group gasoline surrogates," *Energy & Fuels*, vol. 35, no. 4, pp. 3315-3332, 2021.
- [66] E. J. Barrientos and A. L. Boehman, "Examination of the sooting tendency of three-ring aromatic hydrocarbons and their saturated counterparts," *Energy & fuels*, vol. 24, no. 6, pp. 3479-3487, 2010.
- [67] A. Mensch, R. J. Santoro, T. A. Litzinger, and S.-Y. Lee, "Sooting characteristics of surrogates for jet fuels," *Combustion and flame*, vol. 157, no. 6, pp. 1097-1105, 2010.
- [68] C. Zhang, R. Wang, X. Hui, X. Xue, Y. Lin, and C.-J. Sung, "Nonlinear Threshold Sooting Index Prediction Method for Surrogate Formulation Emulating Sooting Characteristics: A Case Study Using RP-3 Jet Fuels," *Energy & Fuels*, vol. 34, no. 8, pp. 9990-9999, 2020.
- [69] Q. Jiao, J. E. Anderson, T. J. Wallington, and E. M. Kurtz, "Smoke point measurements of diesel-range hydrocarbon–oxygenate blends using a novel approach for fuel blend selection," *Energy & Fuels*, vol. 29, no. 11, pp. 7641-7649, 2015.
- [70] V. Iyer *et al.*, "Comparison of Sooting Propensity of JP-8 with its Surrogates in a Wick Burner and a Model Gas Turbine Combustor," in *Fall Technical Meeting of the Eastern States Section of the Combustion Institute 2011*, 2011: Combustion Institute, pp. 311-317.
- [71] D. Kang, D. Kim, V. Kalaskar, A. Boehman, and A. Violi, "Experimental characterization of jet fuels under engine relevant conditions–Part 2: Insights on optimization approach for surrogate formulation," *Fuel*, vol. 239, pp. 1405-1416, 2019.
- [72] B. Graziano, T. Ottenwälder, D. Manderfeld, S. Pischinger, and G. Grünefeld, "Advanced methodology for the detection of smoke point heights in hydrocarbon flames," *Energy & Fuels*, vol. 32, no. 3, pp. 3908-3919, 2018.
- [73] M. L. Botero, S. Mosbach, and M. Kraft, "Sooting tendency and particle size distributions of n-heptane/toluene mixtures burned in a wick-fed diffusion flame," *Fuel*, vol. 169, pp. 111-119, 2016.
- [74] R. J. Watson, M. L. Botero, C. J. Ness, N. M. Morgan, and M. Kraft, "An improved methodology for determining threshold sooting indices from smoke point lamps," *Fuel*, vol. 111, pp. 120-130, 2013.
- [75] A. Mensch, "A study on the sooting tendency of jet fuel surrogates using the threshold soot index," 2009.
- [76] D. Olson, J. Pickens, and R. Gill, "The effects of molecular structure on soot formation II. Diffusion flames," *Combustion and Flame*, vol. 62, no. 1, pp. 43-60, 1985.
- [77] L. Li and P. B. Sunderland, "An improved method of smoke point normalization," *Combustion science and technology*, vol. 184, no. 6, pp. 829-841, 2012.
- [78] S. H. Won *et al.*, "Combustion characteristics of C4 iso-alkane oligomers: Experimental characterization of iso-dodecane as a jet fuel surrogate component," *Combustion and Flame*, vol. 165, pp. 137-143, 2016.

- [79] A. G. Abdul Jameel, N. Naser, A.-H. Emwas, S. Dooley, and S. M. Sarathy, "Predicting fuel ignition quality using ¹H NMR spectroscopy and multiple linear regression," *Energy & Fuels*, vol. 30, no. 11, pp. 9819-9835, 2016.
- [80] S. H. Won *et al.*, "The combustion properties of 2, 6, 10-trimethyl dodecane and a chemical functional group analysis," *Combustion and Flame*, vol. 161, no. 3, pp. 826-834, 2014.
- [81] M. Salamanca, M. L. Botero, J. W. Martin, J. A. Dreyer, J. Akroyd, and M. Kraft, "The impact of cyclic fuels on the formation and structure of soot," *Combustion and Flame*, vol. 219, pp. 1-12, 2020.
- [82] D. Kang, S. Kirby, J. Agudelo, M. Lapuerta, K. Al-Qurashi, and A. L. Boehman, "Combined impact of branching and unsaturation on the autoignition of binary blends in a motored engine," *Energy & fuels*, vol. 28, no. 11, pp. 7203-7215, 2014.
- [83] T. Kathrotia and U. Riedel, "Predicting the soot emission tendency of real fuels—A relative assessment based on an empirical formula," *Fuel*, vol. 261, p. 116482, 2020.
- [84] A. Makwana, S. Iyer, M. Linevsky, R. Santoro, T. Litzinger, and J. O'Connor, "Effects of Fuel Molecular Weight on Emissions in a Jet Flame and a Model Gas Turbine Combustor," *Journal of Engineering for Gas Turbines and Power*, vol. 140, no. 3, 2018.
- [85] C. S. McEnally and L. D. Pfefferle, "Improved sooting tendency measurements for aromatic hydrocarbons and their implications for naphthalene formation pathways," *Combustion and Flame*, vol. 148, no. 4, pp. 210-222, 2007.
- [86] A. B. Amara *et al.*, "Revisiting diesel fuel formulation from Petroleum light and middle refinery streams based on optimized engine behavior," *Fuel*, vol. 174, pp. 63-75, 2016.
- [87] C. S. McEnally and L. D. Pfefferle, "Sooting tendencies of nonvolatile aromatic hydrocarbons," *Proceedings of the Combustion Institute*, vol. 32, no. 1, pp. 673-679, 2009.
- [88] G. D. G. Peña *et al.*, "Effects of methyl group on aromatic hydrocarbons on the nanostructures and oxidative reactivity of combustion-generated soot," *Combustion and Flame*, vol. 172, pp. 1-12, 2016.
- [89] A. Santamaria, N. Yang, E. Eddings, and F. Mondragon, "Chemical and morphological characterization of soot and soot precursors generated in an inverse diffusion flame with aromatic and aliphatic fuels," *Combustion and flame*, vol. 157, no. 1, pp. 33-42, 2010.
- [90] Y. Kobayashi, T. Furuhashi, K. Amagai, and M. Arai, "Soot precursor measurements in benzene and hexane diffusion flames," *Combustion and flame*, vol. 154, no. 3, pp. 346-355, 2008.
- [91] S. M. Sarathy, P. Oßwald, N. Hansen, and K. Kohse-Höinghaus, "Alcohol combustion chemistry," *Progress in energy and Combustion Science*, vol. 44, pp. 40-102, 2014.
- [92] J. Brocard, F. Baronnet, and H. O'Neal, "Chemical kinetics of the oxidation of methyl tert-butyl ether (MTBE)," *Combustion and Flame*, vol. 52, pp. 25-35, 1983.

- [93] B. El Kadi and F. Baronnet, "Study of the oxidation of unsymmetrical ethers (ETBE, TAME) and tentative interpretation of their high octane numbers," *Journal de chimie physique*, vol. 92, pp. 706-725, 1995.
- [94] S. Fischer, F. Dryer, and H. Curran, "The reaction kinetics of dimethyl ether. I: High-temperature pyrolysis and oxidation in flow reactors," *International Journal of Chemical Kinetics*, vol. 32, no. 12, pp. 713-740, 2000.
- [95] Z. Zhu, Z. Li, C. Liu, X. Chen, and S. Liu, "Effects of dimethyl ether on soot formation in premixed laminar flame by laser induced incandescence method," *Journal of Traffic and Transportation Engineering (English Edition)*, vol. 7, no. 3, pp. 312-319, 2020.
- [96] F. Douce, N. Djebaili-Chaumeix, C.-E. Paillard, C. Clinard, and J.-N. Rouzaud, "Soot formation from heavy hydrocarbons behind reflected shock waves," *Proceedings of the Combustion Institute*, vol. 28, no. 2, pp. 2523-2529, 2000.
- [97] A. G. Abdul Jameel, V. C. Oudenhoven, N. Naser, A.-H. M. Emwas, X. Gao, and M. Sarathy, "Predicting ignition quality of oxygenated fuels using artificial neural networks," 2021.
- [98] A. G. Abdul Jameel, "A Comprehensive Model for Cetane Number Prediction Using Machine Learning," in *Turbo Expo: Power for Land, Sea, and Air*, 2021, vol. 84959: American Society of Mechanical Engineers, p. V03BT04A030.
- [99] A. Jameel and A. Gani, "Identification and Quantification of Hydrocarbon Functional Groups in Gasoline Using 1H-NMR Spectroscopy for Property Prediction," *Molecules*, vol. 26, no. 22, p. 6989, 2021.
- [100] F. Alboqami *et al.*, "A Methodology for Designing Octane Number of Fuels Using Genetic Algorithms and Artificial Neural Networks," *Energy & Fuels*, vol. 36, no. 7, pp. 3867-3880, 2022.
- [101] M. A. A. Qasem *et al.*, "A machine learning model for predicting threshold sooting index (TSI) of fuels containing alcohols and ethers," *Fuel*, vol. 322, p. 123941, 2022.
- [102] X. Pei *et al.*, "Swirling flame combustion of heavy fuel oil: Effect of fuel sulfur content," *Journal of Energy Resources Technology*, vol. 143, no. 8, p. 082103, 2021.
- [103] R. M. Pink, *The climate change crisis: Solutions and adaption for a planet in peril*. Springer, 2018.
- [104] V. Thomas, *Climate change and natural disasters: transforming economies and policies for a sustainable future*. Taylor & Francis, 2017.
- [105] S. P. Crossley, W. E. Alvarez, and D. E. Resasco, "Novel micropyrolysis index (mpi) to estimate the sooting tendency of fuels," *Energy & fuels*, vol. 22, no. 4, pp. 2455-2464, 2008.
- [106] M. Saffaripour, P. Zabeti, M. Kholghy, and M. J. Thomson, "An experimental comparison of the sooting behavior of synthetic jet fuels," *Energy & fuels*, vol. 25, no. 12, pp. 5584-5593, 2011.
- [107] D. D. Das *et al.*, "Sooting tendencies of diesel fuels, jet fuels, and their surrogates in diffusion flames," *Fuel*, vol. 197, pp. 445-458, 2017.
- [108] M. P. Hanson and D. Rouvray, "Novel applications of topological indices. 2. Prediction of the threshold soot index for hydrocarbon fuels," *Journal of Physical Chemistry*, vol. 91, no. 11, pp. 2981-2985, 1987.

- [109] N. Ladommatos, P. Rubenstein, and P. Bennett, "Some effects of molecular structure of single hydrocarbons on sooting tendency," *Fuel*, vol. 75, no. 2, pp. 114-124, 1996.
- [110] L. H. Duong, I. K. Reksowardojo, T. H. Soerawidjaja, D. N. Pham, and O. Fujita, "The sooting tendency of aviation biofuels and jet range paraffins: effects of adding aromatics, carbon chain length of normal paraffins, and fraction of branched paraffins," *Combustion Science and Technology*, vol. 190, no. 10, pp. 1710-1721, 2018.
- [111] P. Gokulakrishnan, C. Fuller, M. S. Klassen, and B. V. Kiel, "Ignition characteristics of alternative jet fuels under vitiated conditions," in *50th AIAA/ASME/SAE/ASEE Joint Propulsion Conference*, 2014, p. 3664.
- [112] R. Khare, V. Raghavan, and K. Narayanaswamy, "A chemical kinetic modeling study of the effects of oxygenated species on soot emissions from diesel engines," in *Proceedings of the International Conference on Sustainable Energy and Environmental Challenges*, 2017.
- [113] R. J. Gill, D. B. Olson, and H. F. Calcote, "Correlations of Soot Formation in Turbojet Engines and in Laboratory Flames," AEROCHEM RESEARCH LABS INC PRINCETON NJ, 1983.
- [114] H. Xu, Z. Yang, M. Chaos, and F. Dryer, "Surrogate jet fuel mixture formulation and development of experimental databases," in *JANNAF 42nd Combustion Joint Sub-Committee Meeting Modeling and Data For Combustion Simulation*, Boston Marriott Newton, Hanscom AF Base, Newton, MA, 2008.
- [115] G. Rubio-Gomez, L. Corral-Gomez, J. A. Soriano, A. Gomez, and F. J. Castillo-Garcia, "Vision based algorithm for automated determination of smoke point of diesel blends," *Fuel*, vol. 235, pp. 595-602, 2019.
- [116] F. Battin-Leclerc, "Detailed chemical kinetic models for the low-temperature combustion of hydrocarbons with application to gasoline and diesel fuel surrogates," *Progress in Energy and Combustion Science*, vol. 34, no. 4, pp. 440-498, 2008.
- [117] H. Liu, Z. Wang, Y. Li, Y. Zheng, T. He, and J. Wang, "Recent progress in the application in compression ignition engines and the synthesis technologies of polyoxymethylene dimethyl ethers," *Applied Energy*, vol. 233, pp. 599-611, 2019.
- [118] "ASTM D1322-12, Standard Test Method for Smoke Point of Kerosine and Aviation Turbine Fuel, ASTM International, West Conshohocken, PA, " 2012, doi: www.astm.org.
- [119] A. G. Abdul Jameel, A. M. Elbaz, A.-H. Emwas, W. L. Roberts, and S. M. Sarathy, "Calculation of Average Molecular Parameters, Functional Groups, and a Surrogate Molecule for Heavy Fuel Oils Using ^1H and ^{13}C Nuclear Magnetic Resonance Spectroscopy," *Energy & Fuels*, vol. 30, no. 5, pp. 3894-3905, 2016, doi: 10.1021/acs.energyfuels.6b00303.
- [120] A. M. Elbaz, A. Gani, N. Hourani, A.-H. Emwas, S. M. Sarathy, and W. L. Roberts, "TG/DTG, FT-ICR Mass Spectrometry, and NMR Spectroscopy Study of Heavy Fuel Oil," *Energy & Fuels*, vol. 29, no. 12, pp. 7825-7835, 2015, doi: 10.1021/acs.energyfuels.5b01739.

- [121] A. G. A. Jameel *et al.*, "Heavy fuel oil pyrolysis and combustion: Kinetics and evolved gases investigated by TGA-FTIR," *Journal of analytical and applied pyrolysis*, vol. 127, pp. 183-195, 2017.
- [122] A. G. A. Jameel, N. Naser, A.-H. Emwas, and S. M. Sarathy, "Surrogate formulation for diesel and jet fuels using the minimalist functional group (MFG) approach," *Proceedings of the Combustion Institute*, vol. 37, no. 4, pp. 4663-4671, 2019.
- [123] J. Yu, Y. Ju, and X. Gou, "Surrogate fuel formulation for oxygenated and hydrocarbon fuels by using the molecular structures and functional groups," *Fuel*, vol. 166, pp. 211-218, 2016.
- [124] M. Mehl, W. Pitz, S. Sarathy, and C. Westbrook, "Modeling the combustion of high molecular weight fuels by a functional group approach," *International Journal of Chemical Kinetics*, vol. 44, no. 4, pp. 257-276, 2012.
- [125] D. D. Das, P. C. S. John, C. S. McEnally, S. Kim, and L. D. Pfefferle, "Measuring and predicting sooting tendencies of oxygenates, alkanes, alkenes, cycloalkanes, and aromatics on a unified scale," *Combustion and Flame*, vol. 190, pp. 349-364, 2018.
- [126] A. Violi *et al.*, "Experimental formulation and kinetic model for JP-8 surrogate mixtures," *Combustion Science and Technology*, vol. 174, no. 11-12, pp. 399-417, 2002.
- [127] K. Narayanaswamy, H. Pitsch, and P. Pepiot, "A component library framework for deriving kinetic mechanisms for multi-component fuel surrogates: Application for jet fuel surrogates," *Combustion and Flame*, vol. 165, pp. 288-309, 2016.
- [128] V. R. Iyer *et al.*, "Simulating the sooting propensity of JP-8 with surrogate fuels from hydrocarbon fluids," *Journal of Propulsion and Power*, vol. 30, no. 5, pp. 1410-1418, 2014.
- [129] B. Shukla, A. Miyoshi, and M. Koshi, "Role of methyl radicals in the growth of PAHs," *Journal of the American Society for Mass Spectrometry*, vol. 21, no. 4, pp. 534-544, 2010.
- [130] C. Russo, M. Alfe, J.-N. Rouzaud, F. Stanzione, A. Tregrossi, and A. Ciajolo, "Probing structures of soot formed in premixed flames of methane, ethylene and benzene," *Proceedings of the Combustion Institute*, vol. 34, no. 1, pp. 1885-1892, 2013.
- [131] Y. Liu *et al.*, "Surface functional groups and sp³/sp² hybridization ratios of in-cylinder soot from a diesel engine fueled with n-heptane and n-heptane/toluene," *Fuel*, vol. 179, pp. 108-113, 2016.
- [132] H. Anderson, C. S. McEnally, and L. D. Pfefferle, "Experimental study of naphthalene formation pathways in non-premixed methane flames doped with alkylbenzenes," *Proceedings of the Combustion Institute*, vol. 28, no. 2, pp. 2577-2583, 2000.
- [133] C. S. McEnally and L. D. Pfefferle, "Fuel decomposition and hydrocarbon growth processes for oxygenated hydrocarbons: butyl alcohols," *Proceedings of the Combustion Institute*, vol. 30, no. 1, pp. 1363-1370, 2005.
- [134] P. C. St. John *et al.*, "A quantitative model for the prediction of sooting tendency from molecular structure," *Energy & Fuels*, vol. 31, no. 9, pp. 9983-9990, 2017.

- [135] "Diesel and gasoline," in *Technology collaboration programme on advanced motor fuels* ed: Advanced Motor Fuels by IEA-AMF.
- [136] E. L. Marshall, and Keith Owen, eds, "Motor Gasoline," in *Critical Reports on Applied Chemistry* vol. 34, ed. Cambridge, U.K: Royal Society of Chemistry, 1995.
- [137] E. M. Kurtz, D. Kuhel, J. E. Anderson, and S. A. Mueller, "A comparison of combustion and emissions of diesel fuels and oxygenated fuels in a modern DI diesel engine," *SAE International Journal of Fuels and Lubricants*, vol. 5, no. 3, pp. 1199-1215, 2012.
- [138] X. Li and O. Gulder, "Influence of diesel fuel cetane number and aromatic content on engine exhaust emissions," *Journal of Canadian Petroleum Technology*, vol. 37, no. 11, 1998.
- [139] K. Nakakita *et al.*, "Effect of hydrocarbon molecular structure in diesel fuel on in-cylinder soot formation and exhaust emissions," *SAE transactions*, pp. 1763-1775, 2003.
- [140] M. Natarajan *et al.*, "Oxygenates for advanced petroleum-based diesel fuels: Part 1. Screening and selection methodology for the oxygenates," *SAE Transactions*, pp. 2221-2245, 2001.
- [141] M. A. González D *et al.*, "Oxygenates screening for AdvancedPetroleum-Based Diesel Fuels: Part 2. The Effect of Oxygenate Blending Compounds on Exhaust Emissions," *SAE Transactions*, pp. 2246-2255, 2001.
- [142] R. J. Klein-Douwel *et al.*, "Soot and chemiluminescence in diesel combustion of bio-derived, oxygenated and reference fuels," *Proceedings of the combustion institute*, vol. 32, no. 2, pp. 2817-2825, 2009.
- [143] N. Miyamoto, H. Ogawa, N. M. Nurun, K. Obata, and T. Arima, "Smokeless, low NO_x, high thermal efficiency, and low noise diesel combustion with oxygenated agents as main fuel," *SAE transactions*, pp. 171-177, 1998.
- [144] J. Manin, S. Skeen, L. Pickett, E. Kurtz, and J. E. Anderson, "Effects of oxygenated fuels on combustion and soot formation/oxidation processes," *SAE International Journal of Fuels and Lubricants*, vol. 7, no. 3, pp. 704-717, 2014.
- [145] C. E. Dumitrescu, C. J. Mueller, and E. Kurtz, "Investigation of a tripropylene-glycol monomethyl ether and diesel blend for soot-free combustion in an optical direct-injection diesel engine," *Applied Thermal Engineering*, vol. 101, pp. 639-646, 2016.
- [146] J. Taylor, R. McCormick, and W. Clark, "Non-Petroleum-Based Fuels: Report on the relationship between molecular structure and compression ignition fuels, both conventional and HCCI," National Renewable Energy Lab.(NREL), Golden, CO (United States), 2004.
- [147] D. Siebers, B. Higgins, and L. Pickett, "Flame lift-off on direct-injection diesel fuel jets: oxygen concentration effects," *Sae Transactions*, pp. 1490-1509, 2002.
- [148] J. E. Dec, "A conceptual model of DL diesel combustion based on laser-sheet imaging," *SAE transactions*, pp. 1319-1348, 1997.
- [149] C. J. Mueller, W. J. Pitz, L. M. Pickett, G. C. Martin, D. L. Siebers, and C. K. Westbrook, "Effects of oxygenates on soot processes in DI diesel engines: experiments and numerical simulations," *SAE transactions*, pp. 964-982, 2003.

- [150] C. K. Westbrook, W. J. Pitz, and H. J. Curran, "Chemical kinetic modeling study of the effects of oxygenated hydrocarbons on soot emissions from diesel engines," *The journal of physical chemistry A*, vol. 110, no. 21, pp. 6912-6922, 2006.
- [151] S. Minchin, "Luminous stationary flames: The quantitative relationship between flame dimensions at the sooting point and chemical composition, with special reference to petroleum hydrocarbons," *J. Inst. Petrol. Technol*, vol. 17, no. 88, pp. 102-120, 1931.
- [152] M. A. A. Qasem, E. M. Al-Mutairi, and A. G. A. Jameel, "Smoke point prediction of oxygenated fuels using neural networks," *Fuel*, vol. 332, p. 126026, 2023.
- [153] C. S. McEnally and L. D. Pfefferle, "Sooting tendencies of oxygenated hydrocarbons in laboratory-scale flames," *Environmental science & technology*, vol. 45, no. 6, pp. 2498-2503, 2011.
- [154] L. H. Duong, O. Fujita, I. K. Reksowardojo, T. H. Soerawidjaja, and G. F. Neonufa, "Experimental investigation of the effects of cycloparaffins and aromatics on the sooting tendency and the freezing point of soap-derived biokerosene and normal paraffins," *Fuel*, vol. 185, pp. 855-862, 2016.
- [155] A. Clarke, T. Hunter, and F. Garner, "The tendency to smoke of organic substances on burning, Part I," *J. Inst. Petrol. Technol*, vol. 32, pp. 627-642, 1946.
- [156] R. A. Hunt, "Relation of smoke point to molecular structure," *Industrial & Engineering Chemistry*, vol. 45, no. 3, pp. 602-606, 1953.
- [157] N. K. Cheruiyot *et al.*, "An overview: Polycyclic aromatic hydrocarbon emissions from the stationary and mobile sources and in the ambient air," *Aerosol and Air Quality Research*, vol. 15, no. 7, pp. 2730-2762, 2015.
- [158] R. Barbella, A. Ciajolo, A. d'Anna, and C. Bertoli, "Effect of fuel aromaticity on diesel emissions," *Combustion and flame*, vol. 77, no. 3-4, pp. 267-277, 1989.
- [159] A. D'Anna, M. Alfe, B. Apicella, A. Tregrossi, and A. Ciajolo, "Effect of fuel/air ratio and aromaticity on sooting behavior of premixed heptane flames," *Energy & fuels*, vol. 21, no. 5, pp. 2655-2662, 2007.
- [160] J. Reijnders, M. Boot, and P. de Goey, "Impact of aromaticity and cetane number on the soot-NO_x trade-off in conventional and low temperature combustion," *Fuel*, vol. 186, pp. 24-34, 2016.
- [161] A. D'Anna, A. Ciajolo, M. Alfè, B. Apicella, and A. Tregrossi, "Effect of fuel/air ratio and aromaticity on the molecular weight distribution of soot in premixed n-heptane flames," *Proceedings of the Combustion Institute*, vol. 32, no. 1, pp. 803-810, 2009.
- [162] C. P. West *et al.*, "Molecular composition and the optical properties of brown carbon generated by the ethane flame," *ACS Earth and Space Chemistry*, vol. 4, no. 7, pp. 1090-1103, 2020.
- [163] P. Hellier, M. Talibi, A. Eveleigh, and N. Ladommatos, "An overview of the effects of fuel molecular structure on the combustion and emissions characteristics of compression ignition engines," *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering*, vol. 232, no. 1, pp. 90-105, 2018.

- [164] S. Srihari, B. Chaitanya, and S. Thirumalini, "Experimental study on influence of diphenyl ether and diethyl amine on exhaust emissions of diesel engine," *Materials Today: Proceedings*, vol. 46, pp. 4835-4839, 2021.
- [165] P. Baskar, K. Nanthagopal, and T. Elango, "The effect of two oxygenates on diesel engine emissions," *ARPJ Journal of Engineering and Applied Sciences*, vol. 6, no. 3, pp. 55-60, 2011.
- [166] A. Patil and S. Taji, "Effect of oxygenated fuel additive on diesel engine performance and emission: A review," *IOSR Journal of Mechanical and Civil Engineering (IOSR-JMCE)*, pp. 30-35, 2013.
- [167] A. Patil *et al.*, "Investigation on effect of oxygenated additive on multicylinder diesel engine performance and emission," *International Journal of Innovative Research in Science, Engineering and Technology*, vol. 3, no. 6, pp. 14113-14120, 2014.
- [168] M. A. A. Qasem *et al.*, "A machine learning model for predicting threshold sooting index (TSI) of fuels containing alcohols and ethers," vol. 322, p. 123941, 2022.
- [169] M. Si, Q. Cheng, L. Yuan, Z. Luo, Z. Xu, and H. Zhao, "Physical and chemical characterization of two kinds of coal-derived soot," *Combustion and Flame*, vol. 238, p. 111759, 2022.
- [170] İ. A. Reşitoğlu, K. Altinişik, and A. Keskin, "The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems," *Clean Technologies and Environmental Policy*, vol. 17, no. 1, pp. 15-27, 2015.
- [171] P. Goyal, N. Jaiswal, A. Kumar, J. Dadoo, M. J. T. R. P. D. T. Dwarakanath, and Environment, "Air quality impact assessment of NO_x and PM due to diesel vehicles in Delhi," vol. 15, no. 5, pp. 298-303, 2010.
- [172] R. Palani, A. AbdulGani, and N. Balasubramanian, "Treatment of tannery effluent using a rotating disc electrochemical reactor," *Water Environment Research*, vol. 89, no. 1, pp. 77-85, 2017.
- [173] A. G. Abdul Jameel, A. Alkhateeb, S. Telalović, A. M. Elbaz, W. L. Roberts, and S. M. Sarathy, "Environmental challenges and opportunities in marine engine heavy fuel oil combustion," in *Proceedings of the Fourth International Conference in Ocean Engineering (ICOE2018) Volume 1*, 2019: Springer, pp. 1047-1055.
- [174] F. D. Alboqami, A. A. Pasha, M. I. Alam, A. Abdulraheem, and A. G. Abdul Jameel, "Prediction of Yield Sooting Index Utilizing Artificial Neural Networks and Adaptive-Network-Based Fuzzy Inference Systems," *Arabian Journal for Science and Engineering*, pp. 1-9, 2022.
- [175] J. Pourazar *et al.*, "Diesel exhaust exposure enhances the expression of IL-13 in the bronchial epithelium of healthy subjects," *Respiratory medicine*, vol. 98, no. 9, pp. 821-825, 2004.
- [176] N. Okui and M. Kobayashi, "A Study on Hybrid Control Method for Improvement of Fuel Economy and Exhaust-Gas Emission of Hybrid Trucks," in *JSAE/SAE 2015 International Powertrains, Fuels & Lubricants Meeting*, 2015, no. 2015-01-1780.
- [177] E. C. J. O. J. E. Union, "Commission Regulation (EC) No 692/2008 of 18 July 2008 implementing and amending Regulation (EC) No 715/2007 of the European

- Parliament and of the Council on type-approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information," vol. 199, pp. 1-136, 2008.
- [178] F. M. Graziani, "DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on the promotion of the use of energy from renewable sources (recast)," 2017.
 - [179] B. Bailey, J. Eberhardt, S. Goguen, and J. J. S. t. Erwin, "Diethyl ether (DEE) as a renewable diesel fuel," pp. 1578-1584, 1997.
 - [180] P. Forzatti, L. Lietti, I. Nova, and E. J. C. T. Tronconi, "Diesel NO_x aftertreatment catalytic technologies: Analogies in LNT and SCR catalytic chemistry," vol. 151, no. 3-4, pp. 202-211, 2010.
 - [181] J. Song, M. Alam, A. L. J. C. S. BOEHMAN*, and Technology, "Impact of alternative fuels on soot properties and DPF regeneration," vol. 179, no. 9, pp. 1991-2037, 2007.
 - [182] M. Lapuerta, F. Oliva, J. R. Agudelo, A. L. J. C. Boehman, and Flame, "Effect of fuel on the soot nanostructure and consequences on loading and regeneration of diesel particulate filters," vol. 159, no. 2, pp. 844-853, 2012.
 - [183] X. Pei *et al.*, "Swirling flame combustion of heavy fuel oil: Effect of fuel sulfur content," *Journal of Energy Resources Technology*, vol. 143, no. 8, 2021.
 - [184] F. A. Ruiz, M. Cadrazco, A. F. López, J. Sanchez-Valdepeñas, and J. R. J. F. Agudelo, "Impact of dual-fuel combustion with n-butanol or hydrous ethanol on the oxidation reactivity and nanostructure of diesel particulate matter," vol. 161, pp. 18-25, 2015.
 - [185] O. P. Bhardwaj, B. Lüers, B. Holderbaum, T. Koerfer, S. Pischinger, and M. Honkanen, "Utilization of HVO fuel properties in a high efficiency combustion system: part 2: relationship of soot characteristics with its oxidation behavior in DPF," *SAE International Journal of Fuels and Lubricants*, vol. 7, no. 3, pp. 979-994, 2014.
 - [186] W. Mühlbauer, C. Zöllner, S. Lehmann, S. Lorenz, D. J. C. Brüggemann, and Flame, "Correlations between physicochemical properties of emitted diesel particulate matter and its reactivity," vol. 167, pp. 39-51, 2016.
 - [187] P. Ye *et al.*, "Impact of rail pressure and biodiesel fueling on the particulate morphology and soot nanostructures from a common-rail turbocharged direct injection diesel engine," vol. 17, no. 2, pp. 193-208, 2016.
 - [188] J. A. Soriano, J. R. Agudelo, A. F. López, and O. J. C. Armas, "Oxidation reactivity and nanostructural characterization of the soot coming from farnesane-A novel diesel fuel derived from sugar cane," vol. 125, pp. 516-529, 2017.
 - [189] E. J. I. M. Belenkov, "Formation of graphite structure in carbon crystallites," vol. 37, no. 9, pp. 928-934, 2001.
 - [190] K. Al-Qurashi, A. L. J. C. Boehman, and Flame, "Impact of exhaust gas recirculation (EGR) on the oxidative reactivity of diesel engine soot," vol. 155, no. 4, pp. 675-695, 2008.
 - [191] O. P. Bhardwaj *et al.*, "Utilization of HVO fuel properties in a high efficiency combustion system: part 2: relationship of soot characteristics with its oxidation behavior in DPF," vol. 7, no. 3, pp. 979-994, 2014.

- [192] A. Liati, A. Spiteri, P. Dimopoulos Eggenschwiler, and N. J. J. o. N. R. Vogel-Schäuble, "Microscopic investigation of soot and ash particulate matter derived from biofuel and diesel: implications for the reactivity of soot," vol. 14, no. 11, pp. 1-18, 2012.
- [193] L. Chin-Hsiang, L. Whei-May, and L. J. J. o. E. S. Jiun-Jian, "Morphological and semi-quantitative characteristics of diesel soot agglomerates emitted from commercial vehicles and a dynamometer," vol. 21, no. 4, pp. 452-457, 2009.
- [194] M. B. Fernandes, J. O. Skjemstad, B. B. Johnson, J. D. Wells, and P. J. C. Brooks, "Characterization of carbonaceous combustion residues. I. Morphological, elemental and spectroscopic features," vol. 51, no. 8, pp. 785-795, 2003.
- [195] Y. Ma, M. Zhu, Z. Zhang, and D. J. P. o. t. C. I. Zhang, "Effect of a homogeneous combustion catalyst on the nanostructure and oxidative properties of soot from biodiesel combustion in a compression ignition engine," vol. 35, no. 2, pp. 1947-1954, 2015.
- [196] L. A. Langley, D. E. Villanueva, and D. H. J. C. o. M. Fairbrother, "Quantification of surface oxides on carbonaceous materials," vol. 18, no. 1, pp. 169-178, 2006.
- [197] K. Yehliu, R. L. Vander Wal, O. Armas, A. L. J. C. Boehman, and Flame, "Impact of fuel formulation on the nanostructure and reactivity of diesel soot," vol. 159, no. 12, pp. 3597-3606, 2012.
- [198] V. Gargiulo, M. Alfè, G. Di Blasio, and C. J. F. Beatrice, "Chemico-physical features of soot emitted from a dual-fuel ethanol–diesel system," vol. 150, pp. 154-161, 2015.
- [199] L. Wang, C. Song, J. Song, G. Lv, H. Pang, and W. J. P. o. t. C. I. Zhang, "Aliphatic C–H and oxygenated surface functional groups of diesel in-cylinder soot: Characterizations and impact on soot oxidation behavior," vol. 34, no. 2, pp. 3099-3106, 2013.
- [200] J. R. Agudelo, A. Alvarez, O. J. C. Armas, and Flame, "Impact of crude vegetable oils on the oxidation reactivity and nanostructure of diesel particulate matter," vol. 161, no. 11, pp. 2904-2915, 2014.
- [201] M. A. A. Qasem, E. M. Al-Mutairi, and A. G. A. J. F. Jameel, "Smoke point prediction of oxygenated fuels using neural networks," vol. 332, p. 126026, 2023.
- [202] H. J. J. o. A. S. Burtscher, "Physical characterization of particulate emissions from diesel engines: a review," vol. 36, no. 7, pp. 896-932, 2005.
- [203] A. G. Abdul Jameel, "Predicting sooting propensity of oxygenated fuels using artificial neural networks," *Processes*, vol. 9, no. 6, p. 1070, 2021.
- [204] A. G. A. Jameel *et al.*, "Surrogate formulation and molecular characterization of sulfur species in vacuum residues using APPI and ESI FT-ICR mass spectrometry," *Fuel*, vol. 293, p. 120471, 2021.
- [205] M. Lapuerta, F. J. Martos, and J. M. Herreros, "Effect of engine operating conditions on the size of primary particles composing diesel soot agglomerates," *Journal of aerosol science*, vol. 38, no. 4, pp. 455-466, 2007.
- [206] Y. Jung and C. Bae, "Immaturity of soot particles in exhaust gas for low temperature diesel combustion in a direct injection compression ignition engine," *Fuel*, vol. 161, pp. 312-322, 2015.

- [207] H. Marsh and K. Kuo, "Kinetics and catalysis of carbon gasification," in *Introduction to carbon science*: Elsevier, 1989, pp. 107-151.
- [208] S. Wolff and M. Wang, "Carbon black science & technology," *Marcel Dekker Inc., New York*, 1993.
- [209] R. L. Vander Wal and A. J. Tomasek, "Soot oxidation: dependence upon initial nanostructure," *Combustion and flame*, vol. 134, no. 1-2, pp. 1-9, 2003.
- [210] B. Apicella *et al.*, "Separation and characterization of carbonaceous particulate (soot and char) produced from fast pyrolysis of coal in inert and CO₂ atmospheres," vol. 201, pp. 118-123, 2017.
- [211] H. Mi, X. Zhang, Y. Xu, and F. J. A. S. S. Xiao, "Synthesis, characterization and electrochemical behavior of polypyrrole/carbon nanotube composites using organometallic-functionalized carbon nanotubes," vol. 256, no. 7, pp. 2284-2288, 2010.
- [212] R. M. M. Abbaslou, J. Soltan, and A. K. J. A. C. A. G. Dalai, "Effects of nanotubes pore size on the catalytic performances of iron catalysts supported on carbon nanotubes for Fischer–Tropsch synthesis," vol. 379, no. 1-2, pp. 129-134, 2010.
- [213] M. A. A. Qasem, M. A. Aziz, M. Qamaruddin, J. P. Kim, and S. A. J. C. Onaizi, "Influence of Pamoic Acid as a Complexing Agent in the Thermal Preparation of NiO Nanoparticles: Application to Electrochemical Water Oxidation," vol. 3, no. 2, pp. 573-580, 2018.
- [214] M. A. Ahmed Qasem, M. Aziz, A. S. Hakeem, and S. A. J. C. N. Onaizi, "Preparation of nano-Co₃O₄ by direct thermal decomposition of cobalt (II) nitrate hexahydrate for electrochemical water oxidation," vol. 14, no. 2, pp. 154-159, 2018.
- [215] M. Lapuerta *et al.*, "Analysis of soot from the use of butanol blends in a Euro 6 diesel engine," vol. 33, no. 3, pp. 2265-2277, 2019.
- [216] A. Eftekhari, P. Jafarkhani, and F. J. C. Moztarzadeh, "High-yield synthesis of carbon nanotubes using a water-soluble catalyst support in catalytic chemical vapor deposition," vol. 44, pp. 1298-1352, 2006.
- [217] S.-K. Sze, N. Siddique, J. Sloan, and R. J. A. E. Escribano, "Raman spectroscopic characterization of carbonaceous aerosols," vol. 35, no. 3, pp. 561-568, 2001.
- [218] L. Dombrovsky, S. Sazhin, S. Mikhlovsky, R. Wood, and M. J. F. Heikal, "Spectral properties of diesel fuel droplets," vol. 82, no. 1, pp. 15-22, 2003.
- [219] S. K. Srivastava, V. Vankar, and V. J. T. S. F. Kumar, "Growth and microstructures of carbon nanotube films prepared by microwave plasma enhanced chemical vapor deposition process," vol. 515, no. 4, pp. 1552-1560, 2006.
- [220] M. Lapuerta, F. Oliva, J. R. Agudelo, J. P. J. C. s. Stitt, and technology, "Optimization of Raman spectroscopy parameters for characterizing soot from different diesel fuels," vol. 183, no. 11, pp. 1203-1220, 2011.
- [221] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner, and U. J. C. Pöschl, "Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information," vol. 43, no. 8, pp. 1731-1742, 2005.

- [222] D. Smith and A. Chughtai, "The surface structure and reactivity of black carbon," *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 105, no. 1, pp. 47-77, 1995.
- [223] H. Boehm, "Some aspects of the surface chemistry of carbon blacks and other carbons," *Carbon*, vol. 32, no. 5, pp. 759-769, 1994.
- [224] J.-O. Müller, "Investigations on environmental carbons," Technische Universität Berlin Berlin, 2005.
- [225] M. a. D. Guillén, C. Díaz, and C. G. Blanco, "Characterization of coal tar pitches with different softening points by ¹H NMR: role of the different kinds of protons in the thermal process," *Fuel Processing Technology*, vol. 58, no. 1, pp. 1-15, 1998.
- [226] S. W. Lee and B. Glavincevski, "NMR method for determination of aromatics in middle distillate oils," *Fuel Processing Technology*, vol. 60, no. 1, pp. 81-86, 1999.
- [227] A. G. Abdul Jameel, "Identification and quantification of hydrocarbon functional groups in gasoline using ¹H-NMR spectroscopy for property prediction," *Molecules*, vol. 26, no. 22, p. 6989, 2021.
- [228] A. Santamaria, F. Mondragon, W. Quinonez, E. G. Eddings, and A. F. Sarofim, "Average structural analysis of the extractable material of young soot gathered in an ethylene inverse diffusion flame," *Fuel*, vol. 86, no. 12-13, pp. 1908-1917, 2007.
- [229] L. Wang, C. Song, J. Song, G. Lv, H. Pang, and W. Zhang, "Aliphatic C–H and oxygenated surface functional groups of diesel in-cylinder soot: Characterizations and impact on soot oxidation behavior," *Proceedings of the Combustion Institute*, vol. 34, no. 2, pp. 3099-3106, 2013.
- [230] J. P. Cain, P. L. Gassman, H. Wang, and A. Laskin, "Micro-FTIR study of soot chemical composition—evidence of aliphatic hydrocarbons on nascent soot surfaces," *Physical Chemistry Chemical Physics*, vol. 12, no. 20, pp. 5206-5218, 2010.
- [231] B. Öktem, M. P. Tolocka, B. Zhao, H. Wang, and M. V. Johnston, "Chemical species associated with the early stage of soot growth in a laminar premixed ethylene–oxygen–argon flame," *Combustion and Flame*, vol. 142, no. 4, pp. 364-373, 2005.
- [232] A. Santamaría *et al.*, "FT-IR and ¹H NMR characterization of the products of an ethylene inverse diffusion flame," vol. 146, no. 1-2, pp. 52-62, 2006.
- [233] A. G. Abdul Jameel *et al.*, "Pyrolysis and Oxidation of Waste Tire Oil: Analysis of Evolved Gases," *ACS omega*, vol. 7, no. 25, pp. 21574-21582, 2022.
- [234] P. Guida, A. G. A. Jameel, S. Saxena, and W. L. Roberts, "Fundamental aspects and applications of ultrasonically induced cavitation in heavy fuel oil with a focus on deasphalting, emulsions, and oxidative desulfurization," in *Catalytic and noncatalytic upgrading of oils*: ACS Publications, 2021, pp. 233-293.
- [235] A. Bredin, A. V. Larcher, and B. J. J. T. i. Mullins, "Thermogravimetric analysis of carbon black and engine soot—Towards a more robust oil analysis method," vol. 44, no. 12, pp. 1642-1650, 2011.
- [236] J. Song, M. Alam, A. L. Boehman, U. J. C. Kim, and flame, "Examination of the oxidation behavior of biodiesel soot," vol. 146, no. 4, pp. 589-604, 2006.

- [237] A. Williams, R. L. McCormick, R. R. Hayes, J. Ireland, and H. L. J. S. T. Fang, "Effect of biodiesel blends on diesel particulate filter performance," pp. 563-573, 2006.
- [238] M. A. A. Qasem, A. B. Alquaity, U. Ahmed, E. M. Al-Mutairi, and A. G. A. Jameel, "Characterization of soot emitted from the atmospheric combustion of diethyl ether-diesel blends," *Fuel*, vol. 358, p. 130149, 2024.

Appendix

1. SP model:

```
% This script predicts the smoke point (SP) using artificial neural network
% 10 features of the input and one output are loaded and the network is
% trained to generate a suitable prediction model
%-----

clc;
chos = 0;
out = 1;
NP=10;
possibility=5;
while chos~=possibility,
    chos=menu('MOHAMMED A.Q: Chemical USING NEURAL NETWORK','Load Input File','Load
Target File',...
    'Create And Train','MyTraining','Predction','Exit');
%-----

if chos==1, % This option for loading input file
    [namefile,pathname]=uigetfile('*.','Select Input File');
    if namefile~=0 % check if the input file is selected
        [x,map]=xlsread(strcat(pathname,namefile));
    else
        warndlg('Input File must be selected.','Warning')
```

```

        end

        disp('An Input has just been loaded');
    end

%-----

    if chos==2, % This option for loading target file

        [namefile,pathname]=uigetfile('*. *','Select Target File');

        if namefile~=0 % check if the target file is selected

            [t,map]=xlsread(strcat(pathname,namefile));

        else

            warndlg('Target File must be selected.',' Warning ')

        end

        disp('The Target has just been loaded. ');

    end

%-----

    if chos==3,% Create a nueral netwrok and Train

        [net] = createnn(x',t')

    end

    if chos==4, % This option will train the neural network after selecting the best parameters
    setting

        net=training(x,t)

    end

%-----

    if chos==5, % This option is selected to predict the output of TSI with respect to the input

        prompt={sprintf('%s','X1,X2,X3,X4,..... ')};

        title= ('Please enter the input');

        lines=1;

        def={'0,1,2,3,4,5,6,7,8,9'};

        answer=inputdlg(prompt,title,lines,def);
    end

```

```

        zparameter=double(str2num(char(answer)));
        X =zparameter;

    Y = net(X');%predict(net, X)
    prompt={sprintf('%s','The predicted Output Y ')};
    title= ('Output ');
    lines=1;
    def={num2str(Y) };
    answer=inputdlg(prompt,title,lines,def);
end
%-----
if chos==6, % exit
    break;
end
end
function net=training(x,t)
x=x';
t=t';

trainFcn = 'trainbr'; % Bayesian Regularization backpropagation.

% Create a Fitting Network
hiddenLayerSize = 10;
net = fitnet(hiddenLayerSize,trainFcn);
net.trainParam.goal = 0.00801;
net.divideParam.trainRatio = 70/100;
net.divideParam.valRatio = 15/100;
net.divideParam.testRatio = 15/100;
net.trainParam.mu=0.0265 %i;

```

```

% Train the Network

[net,tr] = train(net,x,t);
x_test = x(:, tr.testInd);

% Test the Network

y_test = net(x_test);
%y_test = y(tr.testInd);
y_test_real = t(tr.testInd);
e = gsubtract(t(tr.testInd),y_test);
performance = perform(net,t(tr.testInd),y_test)

view(net)

end

%-----

function [net] = createnn(P,T)

alphabet = P;

targets = T;

[R,Q] = size(alphabet);

[S2,Q] = size(targets);

S1 = 100;

%S11 = 200;

trainFcn = 'trainbr';

% Create a Fitting Network

hiddenLayerSize = 10;

net = fitnet(hiddenLayerSize,trainFcn);

%trainParam: .showWindow, .showCommandLine, .show, .epochs,

%.time, .goal, .min_grad, .max_fail, .mu, .mu_dec,

%.mu_inc, .mu_max

% Setup Division of Data for Training, Validation, Testing

net.divideParam.trainRatio = 70/100;

net.divideParam.valRatio = 15/100;

```

```

net.divideParam.testRatio = 15/100;

% traingda

%net = newff(minmax(alphabet),[S1 S11 S2],{'tansig' 'tansig' 'tansig'},'traingda');

net = newff(minmax(alphabet),[S1 S2],{'tansig' 'tansig'},'trainbr');

net.LW{2,1}      = net.LW{2,1}*0.01;

net.b{2}         = net.b{2}*0.01;

net.performFcn    = 'mse';

net.trainParam.goal = 0.001;

net.trainParam.show = 20;

net.trainParam.epochs = 500;

net.trainParam.mc   = 0.95;

P                  = alphabet;

T                  = targets;

[net,tr]           = train(net,P,T);

end

%-----

```

2. TSI model:

```

% This script predicts the soot index(TSI)using artificial neural network

% 10 features of the input  and one output are loaded and the network is

% trained to generate a suitable prediction model

%-----

clc;

chos = 0;

out = 1;

NP=10;

possibility=5;

while chos~=possibility,

```

```
chos=menu('MOHAMMED A.Q: Chemical USING NEURAL NETWORK','Load  
Input File','Load Target File',...
```

```
'Create And Train','MyTraining','Predction','Exit');
```

```
%-----
```

```
if chos==1, % This option for loading input file
```

```
    [namefile,pathname]=uigetfile('*.','Select Input File');
```

```
    if namefile~=0 % check if the input file is selected
```

```
        [x,map]=xlsread(strcat(pathname,namefile));
```

```
    else
```

```
        warndlg('Input File must be selected.',' Warning ')
```

```
    end
```

```
    disp('An Input has just been loaded');
```

```
end
```

```
%-----
```

```
if chos==2, % This option for loading target file
```

```
    [namefile,pathname]=uigetfile('*.','Select Target File');
```

```
    if namefile~=0 % check if the target file is selected
```

```
        [t,map]=xlsread(strcat(pathname,namefile));
```

```
    else
```

```
        warndlg('Target File must be selected.',' Warning ')
```

```
    end
```

```
    disp('The Target has just been loaded.');
```

```
end
```

```
%-----
```

```
if chos==3,% Create a nueral netwrok and Train
```

```

    [net] = createnn(x',t')

end

if chos==4, % This option will train the neural network after selecting the best
parameters setting

    net=training(x,t)

end

%-----

if chos==5, % This option is selected to predict the output of TSI with respect to the
input

    prompt={sprintf('%s','X1,X2,X3,X4,..... ')};

    title= ('Please enter the input');

    lines=1;

    def={'0,1,2,3,4,5,6,7,8,9'};

    answer=inputdlg(prompt,title,lines,def);

    zparameter=double(str2num(char(answer)));

    X =zparameter;

    Y = net(X');%predict(net, X)

    prompt={sprintf('%s','The predicted Output Y ')};

    title= ('Output ');

    lines=1;

    def={num2str(Y) };

    answer=inputdlg(prompt,title,lines,def);

end

%-----

if chos==6, % exit

    break;

```

```

end

end

function net=training(x,t)

x=x';

t=t';

trainFcn = 'trainbr'; % Bayesian Regularization backpropagation.

% Create a Fitting Network

hiddenLayerSize = 10;

net = fitnet(hiddenLayerSize,trainFcn);

net.trainParam.goal = 0.00801;

net.divideParam.trainRatio = 70/100;

net.divideParam.valRatio = 15/100;

net.divideParam.testRatio = 15/100;

net.trainParam.mu=0.0265 %i;

% Train the Network

[net,tr] = train(net,x,t);

x_test = x(:, tr.testInd);


% Test the Network

y_test = net(x_test);

%y_test = y(tr.testInd);

y_test_real = t(tr.testInd);

e = gsubtract(t(tr.testInd),y_test);

performance = perform(net,t(tr.testInd),y_test)

view(net)

```

```

end

%-----

function [net] = createnn(P,T)

alphabet = P;

targets = T;

[R,Q] = size(alphabet);

[S2,Q] = size(targets);

S1 = 100;

%S11 = 200;

trainFcn = 'trainbr';

% Create a Fitting Network

hiddenLayerSize = 10;

net = fitnet(hiddenLayerSize,trainFcn);

%trainParam: .showWindow, .showCommandLine, .show, .epochs,

% .time, .goal, .min_grad, .max_fail, .mu, .mu_dec,

% .mu_inc, .mu_max

% Setup Division of Data for Training, Validation, Testing

net.divideParam.trainRatio = 70/100;

net.divideParam.valRatio = 15/100;

net.divideParam.testRatio = 15/100;

% traingda

%net = newff(minmax(alphabet),[S1 S11 S2],{'tansig' 'tansig' 'tansig'},'traingda');

net = newff(minmax(alphabet),[S1 S2],{'tansig' 'tansig'},'trainbr');

net.LW{2,1} = net.LW{2,1}*0.01;

net.b{2} = net.b{2}*0.01;

```

```

net.performFcn      = 'mse';

net.trainParam.goal = 0.001;

net.trainParam.show = 20;

net.trainParam.epochs = 500;

net.trainParam.mc    = 0.95;

P                    = alphabet;

T                    = targets;

[net,tr]             = train(net,P,T);

end

%-----

```

3. OESi model:

```

% providing inputs data for the model
% 12 inputs, 40 samples
inputs = [60.0641268100000 56.6653246900000 52.5746949400000
44.8800325800000 60.4109548100000 58.3340309700000
55.7551930300000 50.6544331800000 60.7380596400000
59.9599025800000 58.9829132200000 57.0144904100000
61.0036461400000 61.2899246300000 61.6482027400000
62.3661959100000 60.5461097700000 59.0035944200000
57.0789139800000 53.2410551600000 20.5007270900000
19.4686432500000 18.2082213600000 15.7816345000000
20.6827989200000 20.3646404100000 19.9650798200000
19.1596888000000 20.9283943400000 21.5988281500000
22.4491894400000 24.1922708900000 21.1754819700000
22.8396472900000 24.9443998800000 29.2377901200000
20.7830143600000 20.8669608500000 20.9728478900000
21.1878634100000
15.7133996200000 14.8242376700000 13.7540864300000 11.7410828100000
16.6390207200000 19.4228037900000 22.8793221400000
29.7160720600000 16.1488867300000 16.9845656600000
18.0337747000000 20.1477046000000 15.7831764200000
15.1535552900000 14.3655831900000 12.7864786800000
16.4369086100000 18.4206522700000 20.8958773300000
25.8315352700000 53.5521274800000 50.8561116300000
47.5636297000000 41.2248843000000 54.4888048000000
55.5067675500000 56.7851799700000 59.3620655000000
54.0971492600000 53.5413894300000 52.8364777300000
51.3915406900000 53.7621976700000 51.8587809700000
49.4514352600000 44.5407989100000 54.3285316000000
54.7046473900000 55.1790661700000 56.1424267700000

```

3.29303605000000	3.10669557500000	2.88242541700000	2.46056295200000
3.30475051100000	3.16178907400000	2.98427925300000	
2.63317732600000	3.30883276900000	3.18135559400000	
3.02130584400000	2.69884012100000	3.30765908000000	
3.17571022700000	3.01057597300000	2.67964516200000	
3.30655674700000	3.17042266400000	3.00056075000000	
2.66185203300000	11.5181010500000	10.9382364500000	
10.2300827100000	8.86673239000000	11.5543001800000	
11.1104769100000	10.5530997500000	9.42959914000000	
11.5669078300000	11.1714865600000	10.6699442200000	
9.64187630200000	11.5632833800000	11.1538926200000	
10.6361157900000	9.57992608300000	11.5598790100000	
11.1374074100000	10.6045171100000	9.52242352500000	
2.25457776200000	2.12699972000000	1.97345311300000	1.68462489600000
2.26259807000000	2.16471949500000	2.04318736200000	
1.80280536100000	2.26539298900000	2.17811571700000	
2.06853762400000	1.84776140500000	2.26458942200000	
2.17425061500000	2.06119141600000	1.83461957300000	
2.26383471000000	2.17063048400000	2.05433449200000	
1.82243750400000	0 0 0	0 0 0	0 0
0 0 0	0 0 0	0 0 0	0 0
0			
12.8876811300000	12.1584159200000	11.2807084700000	9.62970045100000
12.9335270500000	12.3740307600000	11.6793253500000	
10.3052469600000	12.9495034400000	12.4506066300000	
11.8242332400000	10.5622259700000	12.9449100700000	
12.4285128200000	11.7822406300000	10.4871042600000	
12.9405959600000	12.4078193300000	11.7430448900000	
10.4174687700000	8.13914005500000	7.72938508100000	
7.22897598700000	6.26557940600000	8.16471977200000	
7.85109691200000	7.45723244300000	6.66332303500000	
8.17362883100000	7.89420871500000	7.53979930900000	
6.81332636800000	8.17106765100000	7.88177615400000	
7.51589482000000	6.76954992400000	8.16866199000000	
7.87012706200000	7.49356595800000	6.72891637100000	
4.99729793600000	9.84066572900000	15.6699031100000	26.6349662600000
3.72000109800000	3.55907618000000	3.35926178400000	
2.96404297700000	3.72459630200000	3.58110128500000	
3.40094086300000	3.03795647400000	3.72327513500000	
3.57474656200000	3.38862755000000	3.01634961800000	
3.72203429200000	3.56879460300000	3.37758909300000	
2.99632073600000	6.20029649800000	10.4487921100000	
15.6372241500000	25.6260867600000	5.07562501100000	
4.88066032500000	4.63581317700000	4.14227677100000	
5.08116335700000	4.90746091900000	4.68714114100000	
4.23552683900000	5.07957119100000	4.89973217700000	
4.67228083700000	4.20831306700000	5.07807570400000	
4.89249048000000	4.65840002600000	4.18305308500000	
0.134048431000000	0.658939503000000	1.29067237600000	2.47899091600000
0.0709824660000000	0.353856270000000	0.705089995000000	
1.39980557000000	0.205749846000000	1.03076226000000	
2.06657930700000	4.15352722600000	0.179399920000000	
0.897478319000000	1.79615487300000	3.59711229900000	
0.125536893000000	0.627182817000000	1.25311377200000	
2.50123506000000	0.118476585000000	0.586246879000000	

1.15750659200000	2.25730605900000	0.0627108150000000
0.314205001000000	0.630044939000000	1.26668093200000
0.181747467000000	0.914626232000000	1.84419111800000
3.74962512800000	0.158478030000000	0.796518650000000
1.60348033400000	3.24956521700000	0.110900901000000
0.556733668000000	1.11909090900000	2.26102040800000
100.590032800000	102.969009400000	105.985814500000
100.634930300000	103.247372700000	106.686194500000
114.210149500000	99.666745720000	98.352483480000
96.750683200000	93.676825530000	99.865617430000
99.331325300000	98.670658680000	97.372781070000
100.235892700000	101.189735600000	102.405660400000
104.919614100000	168.024888400000	168.123225200000
168.243474300000	168.475465000000	168.490816700000
170.488332300000	173.065023500000	178.503000400000
166.224972500000	159.432371900000	151.576072500000
137.670274900000	166.679119000000	161.564884300000
155.529341000000	144.516811500000	167.558750300000
165.808026900000	163.651226200000	159.439809300000
0.512643561000000	0.563621630000000	0.628267453000000
0.497771236000000	0.488600910000000	0.476529786000000
0.450118824000000	0.493591264000000	0.468316990000000
0.437513139000000	0.378400491000000	0.500000000000000
0.500000000000000	0.500000000000000	0.500000000000000
0.496068455000000	0.480171073000000	0.459905660000000
0.418006431000000	0.518666326000000	0.592418937000000
0.682605736000000	0.856598757000000	0.496703273000000
0.483286322000000	0.465979155000000	0.429453248000000
0.490558364000000	0.454427510000000	0.412638683000000
0.338671675000000	0.500000000000000	0.500000000000000
0.500000000000000	0.500000000000000	0.494194083000000
0.471158248000000	0.442779292000000	0.387365912000000
0.753230000000000	0.766150000000000	0.782300000000000
0.750560000000000	0.752800000000000	0.755600000000000
0.761200000000000	0.749634000000000	0.748170000000000
0.746340000000000	0.742680000000000	0.749900000000000
0.749500000000000	0.749000000000000	0.748000000000000
0.750150000000000	0.750750000000000	0.751500000000000
0.753000000000000	0.852230000000000	0.861150000000000
0.872300000000000	0.894600000000000	0.849560000000000
0.847800000000000	0.845600000000000	0.841200000000000
0.848634000000000	0.843170000000000	0.836340000000000
0.822680000000000	0.848900000000000	0.844500000000000
0.839000000000000	0.828000000000000	0.849150000000000
0.845750000000000	0.841500000000000	0.833000000000000
0.047781314000000	0.072920389000000	0.078053663000000
0.018660876000000	0.043077698000000	0.051501008000000
0.057081831000000	0.128001378000000	0.211341615000000
0.230065764000000	0.240729680000000	0.097609929000000
0.166483834000000	0.182588193000000	0.191868111000000
0.051968776000000	0.098448281000000	0.110839807000000
0.118283909000000	0.055483679000000	0.076011001000000
0.079696678000000	0.081676883000000	0.024179693000000
0.047923709000000	0.054629335000000	0.058738787000000
0.152163741000000	0.222539177000000	0.236194091000000

```

0.243669832000000    0.117120720000000    0.176085843000000
0.187911487000000    0.194440649000000    0.064167937000000
0.105758154000000    0.115081893000000    0.120388683000000
1.33968070800000    0.981639037000000    0.908528700000000    0.867972727000000
2.05149268300000    2.09243362500000    2.10655742400000
2.11591507700000    2.26586172300000    2.42580729600000
2.46174245600000    2.48220851500000    2.20556280600000
2.33635330900000    2.36693524100000    2.38455766600000
2.11574116800000    2.20118796400000    2.22396824500000
2.23765330200000    1.22998026900000    0.937621183000000
0.885128161000000    0.856925227000000    2.06074636700000
2.10055918200000    2.11180285000000    2.11869338000000
2.31223383800000    2.44729752200000    2.47350386700000
2.48785121900000    2.24261350400000    2.35458737800000
2.37704409700000    2.38944287700000    2.13816780900000
2.21462625600000    2.23176679300000    2.24152266700000];
% providing outputs data for the model
% 1 output, 40 samples

```

```

targets = [41.7333333300000    41.7333333300000    43.2089655200000
66.5084210500000    57.2561290300000    53.7218181800000
50.5914285700000    35.8338775500000    26.8303225800000
22.3075675700000    18.1533333300000    16.2320000000000
29.3658064500000    25.8885714300000    24.4318918900000
23.1246153800000    27.6960975600000    22.5200000000000
19.6242105300000    18.9230508500000    33.1604081600000
41.9348717900000    46.8485714300000    49.7521212100000
55.3707692300000    43.8542857100000    42.9560000000000
36.2416949200000    24.6053061200000    23.5988235300000
22.2288888900000    19.9000000000000    33.2015384600000
27.3697872300000    25.6640000000000    24.6361538500000
38.2400000000000    33.1139130400000    27.5218181800000
27.0114285700000];

```

```

% Creating an ANN
hiddenLayerSize = 10;
net = feedforwardnet(hiddenLayerSize);

% Dividing the data into training, validation, and testing sets
net.divideParam.trainRatio = 0.7;
net.divideParam.valRatio = 0.15;
net.divideParam.testRatio = 0.15;

% Training the ANN
[net,tr] = train(net,inputs,targets);

% Testing the ANN
outputs = net(inputs);

% Evaluating performance
performance = perform(net,targets,outputs);

% Plotting training, validation, and testing performance
plotperform(tr)

```

% Predicting output for unknown samples

```

newInputs = [60.0641268100000    56.6653246900000    52.5746949400000
44.8800325800000    60.4109548100000    58.3340309700000
55.7551930300000    50.6544331800000    60.7380596400000
59.9599025800000    58.9829132200000    57.0144904100000
61.0036461400000    61.2899246300000    61.6482027400000
62.3661959100000    60.5461097700000    59.0035944200000
57.0789139800000    53.2410551600000    20.5007270900000
19.4686432500000    18.2082213600000    15.7816345000000
20.6827989200000    20.3646404100000    19.9650798200000
19.1596888000000    20.9283943400000    21.5988281500000
22.4491894400000    24.1922708900000    21.1754819700000
22.8396472900000    24.9443998800000    29.2377901200000
20.7830143600000    20.8669608500000    20.9728478900000
21.1878634100000
15.7133996200000    14.8242376700000    13.7540864300000    11.7410828100000
16.6390207200000    19.4228037900000    22.8793221400000
29.7160720600000    16.1488867300000    16.9845656600000
18.0337747000000    20.1477046000000    15.7831764200000
15.1535552900000    14.3655831900000    12.7864786800000
16.4369086100000    18.4206522700000    20.8958773300000
25.8315352700000    53.5521274800000    50.8561116300000
47.5636297000000    41.2248843000000    54.4888048000000
55.5067675500000    56.7851799700000    59.3620655000000
54.0971492600000    53.5413894300000    52.8364777300000
51.3915406900000    53.7621976700000    51.8587809700000
49.4514352600000    44.5407989100000    54.3285316000000
54.7046473900000    55.1790661700000    56.1424267700000
3.2930360500000    3.1066955750000    2.8824254170000    2.46056295200000
3.3047505110000    3.1617890740000    2.9842792530000
2.6331773260000    3.3088327690000    3.1813555940000
3.0213058440000    2.6988401210000    3.3076590800000
3.1757102270000    3.0105759730000    2.6796451620000
3.3065567470000    3.1704226640000    3.0005607500000
2.6618520330000    11.5181010500000    10.9382364500000
10.2300827100000    8.8667323900000    11.5543001800000
11.1104769100000    10.5530997500000    9.4295991400000
11.5669078300000    11.1714865600000    10.6699442200000
9.6418763020000    11.5632833800000    11.1538926200000
10.6361157900000    9.5799260830000    11.5598790100000
11.1374074100000    10.6045171100000    9.5224235250000
2.2545777620000    2.1269997200000    1.9734531130000    1.6846248960000
2.2625980700000    2.1647194950000    2.0431873620000
1.8028053610000    2.2653929890000    2.1781157170000
2.0685376240000    1.8477614050000    2.2645894220000
2.1742506150000    2.0611914160000    1.8346195730000
2.2638347100000    2.1706304840000    2.0543344920000
1.8224375040000    0      0      0      0      0      0      0      0
0      0      0      0      0      0      0      0      0
0
12.8876811300000    12.1584159200000    11.2807084700000    9.62970045100000
12.9335270500000    12.3740307600000    11.6793253500000
10.3052469600000    12.9495034400000    12.4506066300000
11.8242332400000    10.5622259700000    12.9449100700000

```

12.4285128200000	11.7822406300000	10.4871042600000	
12.9405959600000	12.4078193300000	11.7430448900000	
10.4174687700000	8.13914005500000	7.72938508100000	
7.22897598700000	6.26557940600000	8.16471977200000	
7.85109691200000	7.45723244300000	6.66332303500000	
8.17362883100000	7.89420871500000	7.53979930900000	
6.81332636800000	8.17106765100000	7.88177615400000	
7.51589482000000	6.76954992400000	8.16866199000000	
7.87012706200000	7.49356595800000	6.72891637100000	
4.99729793600000	9.84066572900000	15.6699031100000	26.6349662600000
3.72000109800000	3.55907618000000	3.35926178400000	
2.96404297700000	3.72459630200000	3.58110128500000	
3.40094086300000	3.03795647400000	3.72327513500000	
3.57474656200000	3.38862755000000	3.01634961800000	
3.72203429200000	3.56879460300000	3.37758909300000	
2.99632073600000	6.20029649800000	10.4487921100000	
15.6372241500000	25.6260867600000	5.07562501100000	
4.88066032500000	4.63581317700000	4.14227677100000	
5.08116335700000	4.90746091900000	4.68714114100000	
4.23552683900000	5.07957119100000	4.89973217700000	
4.67228083700000	4.20831306700000	5.07807570400000	
4.89249048000000	4.65840002600000	4.18305308500000	
0.134048431000000	0.658939503000000	1.290672376000000	2.478990916000000
0.0709824660000000	0.3538562700000000	0.7050899950000000	
1.399805570000000	0.2057498460000000	1.030762260000000	
2.066579307000000	4.153527226000000	0.1793999200000000	
0.8974783190000000	1.796154873000000	3.597112299000000	
0.1255368930000000	0.6271828170000000	1.253113772000000	
2.501235060000000	0.1184765850000000	0.5862468790000000	
1.157506592000000	2.257306059000000	0.0627108150000000	
0.3142050010000000	0.6300449390000000	1.266680932000000	
0.1817474670000000	0.9146262320000000	1.844191118000000	
3.749625128000000	0.1584780300000000	0.7965186500000000	
1.603480334000000	3.249565217000000	0.1109009010000000	
0.5567336680000000	1.119090909000000	2.261020408000000	
100.5900328000000	102.9690094000000	105.9858145000000	112.1675036000000
100.6349303000000	103.2473727000000	106.6861945000000	
114.2101495000000	99.6667457200000	98.3524834800000	
96.7506832000000	93.6768255300000	99.8656174300000	
99.3313253000000	98.6706586800000	97.3727810700000	
100.2358927000000	101.1897356000000	102.4056604000000	
104.9196141000000	168.0248884000000	168.1232252000000	
168.2434743000000	168.4754650000000	168.4908167000000	
170.4883323000000	173.0650235000000	178.5030004000000	
166.2249725000000	159.4323719000000	151.5760725000000	
137.6702749000000	166.6791190000000	161.5648843000000	
155.5293410000000	144.5168115000000	167.5587503000000	
165.8080269000000	163.6512262000000	159.4398093000000	
0.5126435610000000	0.5636216300000000	0.6282674530000000	0.760732221000000
0.4977712360000000	0.4886009100000000	0.4765297860000000	
0.4501188240000000	0.4935912640000000	0.4683169900000000	
0.4375131390000000	0.3784004910000000	0.5000000000000000	
0.5000000000000000	0.5000000000000000	0.5000000000000000	
0.4960684550000000	0.4801710730000000	0.4599056600000000	
0.4180064310000000	0.5186663260000000	0.5924189370000000	

0.682605736000000	0.856598757000000	0.496703273000000	
0.483286322000000	0.465979155000000	0.429453248000000	
0.490558364000000	0.454427510000000	0.412638683000000	
0.338671675000000	0.500000000000000	0.500000000000000	
0.500000000000000	0.500000000000000	0.494194083000000	
0.471158248000000	0.442779292000000	0.387365912000000	
0.753230000000000	0.766150000000000	0.782300000000000	0.814600000000000
0.750560000000000	0.752800000000000	0.755600000000000	
0.761200000000000	0.749634000000000	0.748170000000000	
0.746340000000000	0.742680000000000	0.749900000000000	
0.749500000000000	0.749000000000000	0.748000000000000	
0.750150000000000	0.750750000000000	0.751500000000000	
0.753000000000000	0.852230000000000	0.861150000000000	
0.872300000000000	0.894600000000000	0.849560000000000	
0.847800000000000	0.845600000000000	0.841200000000000	
0.848634000000000	0.843170000000000	0.836340000000000	
0.822680000000000	0.848900000000000	0.844500000000000	
0.839000000000000	0.828000000000000	0.849150000000000	
0.845750000000000	0.841500000000000	0.833000000000000	
0.047781314000000	0.072920389000000	0.078053663000000	0.080901208000000
0.018660876000000	0.043077698000000	0.051501008000000	
0.057081831000000	0.128001378000000	0.211341615000000	
0.230065764000000	0.240729680000000	0.097609929000000	
0.166483834000000	0.182588193000000	0.191868111000000	
0.051968776000000	0.098448281000000	0.110839807000000	
0.118283909000000	0.055483679000000	0.076011001000000	
0.079696678000000	0.081676883000000	0.024179693000000	
0.047923709000000	0.054629335000000	0.058738787000000	
0.152163741000000	0.222539177000000	0.236194091000000	
0.243669832000000	0.117120720000000	0.176085843000000	
0.187911487000000	0.194440649000000	0.064167937000000	
0.105758154000000	0.115081893000000	0.120388683000000	
1.33968070800000	0.98163903700000	0.90852870000000	0.86797272700000
2.05149268300000	2.09243362500000	2.10655742400000	
2.11591507700000	2.26586172300000	2.42580729600000	
2.46174245600000	2.48220851500000	2.20556280600000	
2.33635330900000	2.36693524100000	2.38455766600000	
2.11574116800000	2.20118796400000	2.22396824500000	
2.23765330200000	1.22998026900000	0.93762118300000	
0.88512816100000	0.85692522700000	2.06074636700000	
2.10055918200000	2.11180285000000	2.11869338000000	
2.31223383800000	2.44729752200000	2.47350386700000	
2.48785121900000	2.24261350400000	2.35458737800000	
2.37704409700000	2.38944287700000	2.13816780900000	
2.21462625600000	2.23176679300000	2.24152266700000]; % unknown	

```

samples
predictedOutputs = net(newInputs);
disp('Predicted outputs for new samples:');
disp(predictedOutputs);

```

Vitae

Name : Mohammed Ameen Ahmed Qasem |

Nationality : Yemeni |

Date of Birth : 1/1/1987 |

Email : mohammedameen2030@gmail.com |

Address : Dhohrh Village, Al Sayyani District, Ibb Governorate, Yemen, 00967 |

Academic Background

- PhD in Chemical engineering, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, KSA, (Jan,2018-Jan,2024).
- MS in Chemical engineering, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, KSA, (Sep,2015-Dec,2017).
- BS in Chemical engineering, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, KSA, (Sep,2009-Jan,2015).

Outcome of the Work

- Qasem, Mohammed Ameen Ahmed, et al. "Characterization of soot emitted from the atmospheric combustion of diethyl ether-diesel blends." Fuel 358 (2024): 130149.
- Qasem, Mohammed Ameen Ahmed, Eid M. Al-Mutairi, and Abdul Gani Abdul Jameel. "Smoke point prediction of oxygenated fuels using neural networks." Fuel 332 (2023): 126026.
- Qasem, Mohammed Ameen Ahmed, et al. "A machine learning model for predicting threshold sooting index (TSI) of fuels containing alcohols and ethers." Fuel 322 (2022): 123941.
- Qasem, Mohammed Ameen Ahmed, et al. "Sooting Propensity Trends for Diesel/Gasoline-Ether Blends and Their Prediction Using ANN" (under preparation)