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Predicting Enthalpy of Combustion Using Machine Learning

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Abstract: The present work discusses the development and application of a machine-learning-based model to predict the enthalpy of combustion of various oxygenated fuels of interest. A detailed dataset containing 207 pure compounds and 38 surrogate fuels has been prepared, representing various chemical classes, namely paraffins, olefins, naphthenes, aromatics, alcohols, ethers, ketones, and aldehydes. The dataset was subsequently used for constructing an artificial neural network (ANN) model with 14 input layers, 26 hidden layers, and 1 output layer for predicting the enthalpy of combustion for various oxygenated fuels. The ANN model was trained using the collected dataset, validated, and finally tested to verify its accuracy in predicting the enthalpy of combustion. The results for various oxygenated fuels are discussed, especially in terms of the influence of different functional groups in shaping the enthalpy of combustion values. In predicting the enthalpy of combustion, 96.3% accuracy was achieved using the ANN model. The developed model can be successfully employed to predict the enthalpies of neat compounds and mixtures as the obtained percentage error of 4.2 is within the vicinity of experimental uncertainty.

Keywords: enthalpy of combustion; machine learning; functional groups; oxygenated fuels

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1. Introduction

Thermochemistry is a subfield of chemical thermodynamics that studies the interactions of heat, work, and other forms of energy in the context of chemical and physical processes. When a system undergoes a change of state, its internal energy, enthalpy, and associated properties change to account for the energy transfer between the system and the surroundings. All heat engines around us, including steam power plants, gas power plants, and automobiles, operate by converting the chemical energy of the fuel into thermal energy, which is subsequently converted to the desired end-use form. In this regard, the enthalpy of combustion is defined as the quantum of change in enthalpy when any element/compound undergoes complete oxidation at a given temperature and pressure. Enthalpies of combustion for various substances are typically measured using a bomb calorimeter (see Figure 1). However, measuring the enthalpy of combustion of various fuels, fuel blends, and surrogates is a time-consuming and costly procedure which necessitates the use of alternate approaches. Among the various possible approaches, the use of machine learning to predict the enthalpy of combustion is promising and has been explored extensively in this work.

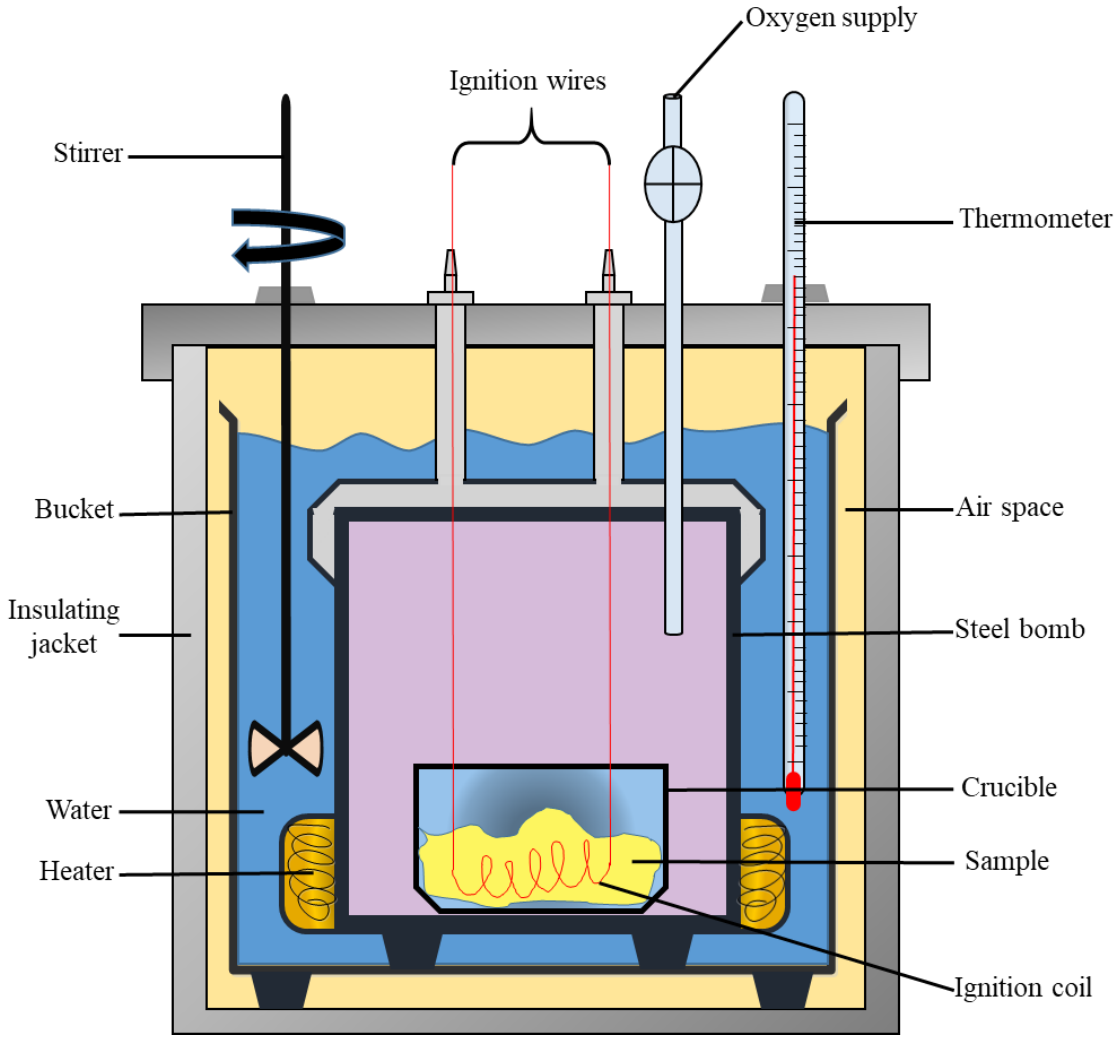

Figure 1. A cross-sectional view of typical bomb calorimeter.

Machine-learning tools help in predicting the enthalpy of combustion for various fuels once they have been rigorously tested over a predefined dataset. A number of machine-learning algorithms have been developed over the years, such as decision trees, random forests, Naïve Bayes, support vector machines, k-means, etc. Neural networks are a subset of machine learning and are at the heart of deep learning algorithms. Typical machine-learning methods are based on the use of neural networks with one or more layers connecting the desired output to the given input. A neural network is a set of algorithms that attempts to detect underlying relationships in a piece of data using a technique similar to the way that the human brain works. In this context, neural networks are systems of neurons that might be biological or artificial in origin. Due to their excellent adaptability to changing inputs, neural networks are widely being used to obtain the best possible results without the need to change the output criterion. Artificial neural networks (ANNs) have therefore been used in this study to develop the required machine-learning tools.

The use of ANNs for predicting the enthalpy of combustion is rather novel. The few relevant studies that have utilized multiple approaches for developing predictive models for the estimation of the enthalpy of combustion are discussed here. Gharagheizi et al. [1] developed an ANN-based model to predict the enthalpy of combustion of various pure compounds using the group-contribution method. A squared correlation coefficient of 0.99999 with a root-mean-squared error of 12.57 kJ/mol, in comparison with experimental values from the literature, was reported. Albahri [2] also used the group-contribution method for predicting the enthalpy of combustion; however, a multivariable nonlinear-regression-

based method was used for this purpose. The enthalpy of combustion was predicted based on the molecular structure, with a reported average error of 0.71%. Recently, Dashti et al. [3] compared three different models, namely a least-squares support-vector machine, genetic programming, and an adaptive neuro-fuzzy inference system, for predicting the enthalpy of combustion of several chemical compounds. It was concluded that the particle swarm optimization–adaptive neuro-fuzzy inference system (PSO–ANFIS) model with four inputs was the most accurate among the three models. The ANFIS structure contains five layers: 1: the fuzzification layer; 2: the IF layer; 3: the normalization layer; 4: the THEN layer; and 5: the summation layer. In this model, MF variables should be estimated immediately after the generation of the initial FIS model and the training of the ANFIS. The MF values are adjusted via PSO algorithms to find the finest structure [3].

This study reports a detailed ANN model to predict the enthalpy of combustion of compounds (neat and mixtures) and real fuels belonging to different chemical families. The functional groups present in the fuels are used as input features to the ANN model. The method of using functional groups for predicting fuel properties has been reported in a number of recent studies [4–6]. Functional groups present in the fuels are also relevant for surrogate formulation [7], particulate matter formation [8–11], and property prediction [12–14].

2. Theoretical Background

The enthalpy of combustion is calculated using the data from the bomb calorimeter using Equation (1):

$$\Delta H_c = m \times C_p \times \Delta T \quad (1)$$

where ΔH_c is the enthalpy of combustion in kJ, m is the mass of water in kg, C_p is the specific heat capacity of water in kJ/kg °C, and ΔT is the temperature change of water in °C. After obtaining these enthalpies of combustion from the literature, each compound was defined with a specific variable according to a convention so that the machine could relate the given enthalpy of combustion to the corresponding compound. To define each compound, 13 variables were assigned to each compound. These variables, along with their definitions, are presented in Table 1.

Table 1. Variables, along with their definitions.

No.	Variables	Definitions
1	P.CH3 (wt %)	Weight percentage of paraffinic CH_3 groups in the compound
2	P.CH2 (wt %)	Weight percentage of paraffinic CH_2 groups in the compound
3	P.CH (wt %)	Weight percentage of paraffinic CH groups in the compound
4	Olef (wt %)	Weight percentage of olefin groups in the compound
5	Naph (wt %)	Weight percentage of naphthene groups in the compound
6	Arom (wt %)	Weight percentage of aromatic groups in the compound
7	Alc OH (wt %)	Weight percentage of alcohol groups in the compound
8	Ether O (wt %)	Weight percentage of ether groups in the compound
9	Aldeh CHO (wt %)	Weight percentage of aldehyde groups in the compound
10	Ketone CO (wt %)	Weight percentage of ketone groups in the compound
11	Ester (wt %)	Weight percentage of ester groups in the compound
12	Mol wt	Molecular weight of the compound
13	BI	Branching index of the compound

BI refers to the branching index of the molecule or mixture. It represents the degree of branching/linearity of a molecule, while including the impact of paraffinic branches on the longest chain present in the molecule. More information related to BI has been reported here [15,16].

3. Dataset and Machine Learning

The dataset was built using the collection of data from the extensive available literature on the enthalpy of combustion that meets the criteria that all data should be at the same condition (i.e., temperature and pressure) and that the method used to obtain these enthalpies should be consistent (i.e., bomb calorimeter method).

After the collection of all the possible data, Tables 2 and S1–S10 were generated. Tables S1–S10 are provided in the Supplementary Materials. Table 2 shows the enthalpy of combustion for 204 compounds from the literature. Edwards and Maurice (2001) [17], estimated the enthalpy of combustion for five surrogates (S1–S5), containing a total of 38 compounds, as shown in Table S1. Similarly, Huber et al. (2009) [18] reported the enthalpy of combustion for two surrogates (S6 and S7), consisting of a total of five compounds, as shown in Table S2. Table S3 represents the enthalpy of combustion for six surrogates (S8–S13), containing a total of five components, as studied by Shrestha (2014) [19]. Similarly, Kalghatgi et al. (2011) [20] calculated the enthalpy of combustion for three surrogates (S14–S16), containing a total of three compounds, as shown in Table S4. Table S5 shows the enthalpy of combustion for two surrogates (S17–S18), comprising a total of nine components, as studied by Huber et al. (2010) [21]. In a same way, Eddings et al. (2005) [22] estimated the enthalpy of combustion for two surrogates (S19–S20), containing a total of six compounds, as shown in Table S6. Table S7 shows the enthalpy of combustion for two surrogates (S21, S22), comprising a total of three fuel constituents, as studied by Naik et al. (2010) [23]. Grubinger et al. (2021) [24] estimated the enthalpy of combustion for three surrogates (S23–S25), containing a total of 11 compounds, as shown in Table S8. Similarly, Table S9 shows the enthalpy of combustion for 9 surrogates (S26–S34), containing a total of 17 compounds, as reported by Xu et al. (2015) [25]. Grubinger et al. (2021) [24] reported the enthalpy of combustion for four surrogates (S35–S38), containing a total of six compounds, as shown in Table S10.

Table 2. Enthalpy of combustion of different compounds from the literature.

Sr. No.	Compound Name	Compound Formula	Enthalpy of Combustion (Kcal/mol)	References
1	Ethane	C_2H_6	372.82	[26]
2	Propane	C_3H_8	530.605	
3	n-Butane	C_4H_{10}	687.982	
4	n-Pentane	C_5H_{12}	838.8	
5	n-Hexane	C_6H_{14}	995.01	
6	n-Heptane	C_7H_{16}	1151.27	
7	n-Octane	C_8H_{18}	1307.53	
8	n-Nonane	C_9H_{20}	1463.3	
9	n-Decane	$C_{10}H_{22}$	1620.06	
10	n-Undecane	$C_{11}H_{24}$	1776.32	
11	n-Dodecane	$C_{12}H_{26}$	1932.59	
12	n-Hexadecane	$C_{16}H_{34}$	2557.64	
13	2-Methylpropane	C_4H_{10}	686.342	
14	2-Methylbutane	C_5H_{12}	837.3	
15	2,2-Dimethylpropane	C_5H_{12}	840.49	
16	2-Methylpentane	C_6H_{14}	993.71	
17	3-Methylpentane	C_6H_{14}	994.25	
18	2,2-Dimethylbutane	C_6H_{14}	991.52	
19	2,3-Dimethylbutane	C_6H_{14}	993.05	
20	2-Methylhexane	C_7H_{16}	1149.97	
21	3-Methylhexane	C_7H_{16}	1150.55	
22	3-Ethylpentane	C_7H_{16}	1151.13	
23	2,2-Dimethylpentane	C_7H_{16}	1147.85	
24	2,3-Dimethylpentane	C_7H_{16}	1149.09	
25	2,4-Dimethylpentane	C_7H_{16}	1148.73	
26	3,3-Dimethylpentane	C_7H_{16}	1148.83	

Table 2. *Cont.*

Sr. No.	Compound Name	Compound Formula	Enthalpy of Combustion (Kcal/mol)	References
27	2,2,3-Trimethylbutane	C_7H_{16}	1148.27	
28	2-Methylheptane	C_8H_{18}	1306.28	
29	3-Methylheptane	C_8H_{18}	1306.92	
30	4-Methylheptane	C_8H_{18}	1307.09	
31	3-Ethylhexane	C_8H_{18}	1307.39	
32	2,2-Dimethylhexane	C_8H_{18}	1304.64	
33	2,3-Dimethylhexane	C_8H_{18}	1306.86	
34	2,4-Dimethylhexane	C_8H_{18}	1305.8	
35	2,5-Dimethylhexane	C_8H_{18}	1305	
36	3,3-Dimethylhexane	C_8H_{18}	1305.68	
37	3,4-Dimethylhexane	C_8H_{18}	1307.04	
38	2-Methyl-3-ethylpentane	C_8H_{18}	1307.58	
39	3-Methyl-3-ethylpentane	C_8H_{18}	1306.8	
40	2,2,3-Trimethylpentane	C_8H_{18}	1305.83	
41	2,2,4-Trimethylpentane	C_8H_{18}	1305.29	
42	2,3,3-Trimethylpentane	C_8H_{18}	1306.64	
43	2,3,4-Trimethylpentane	C_8H_{18}	1306.28	
44	2,2,3,3-Tetramethylbutane	C_8H_{18}	1303.03	
45	n-Tridecane	$C_{13}H_{28}$	2088.85	
46	n-Tetradecane	$C_{14}H_{30}$	2245.11	
47	n-Pentadecane	$C_{15}H_{32}$	2401.37	
48	n-Heptadecane	$C_{17}H_{36}$	2713.9	
49	n-Octadecane	$C_{18}H_{38}$	2870.16	
50	n-nonadecane	$C_{19}H_{40}$	3026.43	
51	n-Eicosane	$C_{20}H_{42}$	3182.69	
52	Ethylene	C_2H_4	337.25	
53	Propylene	C_3H_6	419.9	
54	n-1-Butene	C_4H_8	649.66	
55	n-1-Pentene	C_5H_{10}	806.78	
56	n-1-Hexene	C_6H_{12}	963.9	[27]
57	n-1-Heptene	C_7H_{14}	1120.9	
58	n-1-Octene	C_8H_{16}	1277.97	
59	n-1-Nonene	C_9H_{18}	1434.9	
60	n-1-Decene	$C_{10}H_{20}$	1591.95	
61	Benzene	C_6H_6	3267.49	
62	Toluene	C_7H_8	3909.9	[28]
63	Naphthalene	C_9H_{10}	5157	
64	2-Methyl-2-butene	$C_{13}H_{12}$	3362.2	[29]
65	1-Methyl-1-cyclohexene	C_7H_{12}	4353	
66	1-Pentanol	$C_5H_{12}O$	3329.96	
67	1-Octanol	$C_8H_{18}O$	5292.5	[30]
68	1-Butanol	$C_4H_{10}O$	2675.61	
69	1-Decanol	$C_{10}H_{22}O$	10,468.26	
70	1,2,3-trimethylcyclohexane	$C_{12}H_{10}O_2$	5837.7	
71	Ethylcyclohexane	$C_{12}H_{10}O_2$	5059.1	
72	methylcyclohexane	$C_{12}H_{10}O_2$	4565.9	
73	2-Methylheptane	$C_{12}H_{10}O_2$	5464.7	
74	Bicyclohexane	C_6H_{10}	3818.8	
75	1,3-Dimethylcyclopentane	C_7H_{14}	4561.3	
76	1,2,4-Trimethylcyclopentane	C_8H_{16}	5208.3	
77	1,1-Dimethylcyclohexane	C_8H_{16}	5196.1	
78	1,3-Dimethylcyclohexane	C_8H_{16}	5177.3	
79	1,4-Dimethylcyclohexane	C_8H_{16}	5138.8	
80	1,2,3-Trimethylcyclohexane	C_9H_{18}	5837.7	

Table 2. *Cont.*

Sr. No.	Compound Name	Compound Formula	Enthalpy of Combustion (Kcal/mol)	References
81	1,3,3-Trimethylcyclohexane	C_9H_{18}	5832.6	
82	3,3-Dimethylcyclohexene	C_9H_{18}	4995.4	
83	Bicycloheptane	C_7H_{12}	4308.7	
84	Ethylenecyclohexane	$C_{10}H_{18}$	5059.1	
85	Isopropyl-1-cyclohexene-1	C_9H_{16}	5611.2	
86	o-Xylene	C_8H_{10}	4578.1	
87	m-Xylene	C_8H_{10}	4567.7	
88	p-Xylene	C_8H_{10}	4556.8	
89	Diamylene	$C_{10}H_{20}$	6616.8	
90	1-methyl-3-cyclohexene	C_7H_{12}	4364.3	
91	Phenyl-1-butene-2	$C_{10}H_{12}$	5702.1	
92	Isopropyl alcohol	C_3H_3O	1985.6	
93	Ethylvinyl carbinol	$C_5H_{10}O$	3148.6	
94	Pinacolyl alcohol	$C_6H_{14}O$	3925.2	
95	1,3-Dimethylcyclohexanol-5	$C_8H_{16}O$	4949	
96	Trimethyl carbinol	$C_4H_{10}O$	2631.7	
97	Dimethylethyl carbinol	$C_5H_{12}O$	3281.2	
98	1,3-Dimethylcyclohexanol-2	$C_8H_{16}O$	5001.7	
99	2-Methyl-2-propanol	$C_4H_{10}O$	2631.7	
100	Ethylene glycol	$C_2H_6O_2$	1179.8	
101	Propylene glycol	$C_3H_8O_2$	1802.4	
102	Phenol	C_6H_6O	3064.3	
103	Glycerol	$C_3H_8O_2$	1661.5	
104	Anisole	C_7H_8O	3787.8	
105	Phenetole	$C_8H_{10}O$	4423.1	
106	m-Cresol methyl ether	$C_8H_{10}O$	4423.6	
107	Safrole	$C_{10}H_{10}O_2$	5206.6	
108	Isosafrole	$C_{10}H_{10}O_2$	5163.9	[29]
109	Acenaphthene	$C_{12}H_{10}$	6241.1	
110	Phenyl-1-butene-2	$C_{12}H_{10}$	5702.1	
111	Phenyl-1-pentene-2	$C_{11}H_{14}$	6325.4	
112	Benzil	$C_{14}H_{10}O_2$	6789.9	
113	Benzoin	$C_{14}H_{10}O_2$	6994.8	
114	Furfuraldehyde	$C_5H_4O_2$	2339.8	
115	1-Naphthalenol	$C_{10}H_8O$	4960.9	
116	Vinyl acetate	$C_4H_5O_2$	2084.5	
117	Ethylcycloheptane	C_9H_{18}	5883.2	
118	1-Methyl-3-propylcyclohexane	$C_{10}H_{20}$	6285.1	
119	Ethyl-1-cyclohexene-1	C_8H_{14}	5042.3	
120	1-Isopropyl-1-cyclohexene	C_9H_{16}	5611.2	
121	Methylenecyclohexane	C_7H_{12}	4404.3	
122	Propyl benzoate	$C_{10}H_{12}O_2$	5250.1	
123	1-Methylcyclohexane-1,2-diol	$C_7H_{14}O_2$	4164.5	
124	Diphenylstyrene	$C_{20}H_{16}$	10,493.5	
125	Amyl benzoate	$C_{12}H_{16}O$	6568.4	
126	Cycloheptene	C_7H_{12}	4390.7	
127	1,2-Propadiene	C_3H_4	1962.05	
128	Eugenol acetate	$C_{12}H_{14}O_3$	6268.3	
129	Phenyl benzoate	$C_{13}H_{10}O_2$	6321.4	
130	Isopropyltoluene	C_7H_8	5895.9	
131	1,2,4-trimethylbenzene	$C_5H_{10}O$	5195.3	
132	Cyclohexanol	C_6H_{12}	3724.9	
133	Cyclopentanone	C_7H_{14}	2852.1	
134	Isopropenylbenzene	$C_{16}H_{32}$	5218.7	
135	Propylbenzene	$C_{18}H_{36}$	5214.9	
136	Styrene	$C_{13}H_{26}$	4375	

Table 2. *Cont.*

Sr. No.	Compound Name	Compound Formula	Enthalpy of Combustion (Kcal/mol)	References
137	Cyclohexane	C_6H_{12}	3919.8	[31]
138	Methyl cyclohexane	C_7H_{14}	4564.3	
139	Ethyl cyclohexane	C_8H_{16}	5222.6	
140	Propyl cyclohexane	C_9H_{18}	5875.8	
141	1,1-Dimethyl cyclohexane	C_8H_{16}	5216	
142	1,2-Dimethyl cyclohexane	C_8H_{16}	5216.5	
143	Cyclopentane	C_5H_{10}	3291.6	
144	Propyl cyclopentane	C_8H_{16}	5245.6	
145	Butyl cyclopentane	C_9H_{18}	5899.9	
146	Decyl cyclopentane	$C_{15}H_{30}$	9822.1	
147	1,1-Dimethyl cyclopentane	C_7H_{14}	4583.3	
148	1,2-Dimethyl cyclopentane	C_7H_{14}	4561.3	
149	2-Hexanone	$C_6H_{12}O$	3754.02	[32]
150	3-Hexanone	$C_6H_{12}O$	3755.9	
151	3,3-Dimethylbutan-2-one	$C_6H_{12}O$	3347.49	
152	5-Nonanone	$C_9H_{18}O$	5715.81	
153	6-Undecanone	$C_{11}H_{22}O$	7024.6	
154	2-Pentanone	$C_5H_{10}O$	3099.41	
155	3-Pentanone	$C_5H_{10}O$	3100.19	
156	Cyclohexene	C_6H_{10}	895.27	[33]
157	1-Methylcyclopentene	C_6H_{10}	895.69	
158	Cyclohexyl-benzene	$C_{12}H_{16}$	6922.73	[34]
159	Phenylbenzene	$C_{12}H_{10}O_2$	6245.45	
160	Cyclohexyl-cyclohexane	$C_{12}H_{22}$	7578.83	
161	Ethylbenzene	C_8H_{10}	4563.9	[35]
162	Propylbenzene	C_9H_{12}	5218	
163	1,2-Dimethylbenzene	C_8H_{10}	4552.6	
164	1,3-Dimethylbenzene	C_8H_{10}	4551.6	
165	1,4-Dimethylbenzene	C_8H_{10}	4552.6	
166	Heptyl cyclohexane	$C_{13}H_{26}$	8478.5	
167	Methanol	CH_4O	726	
168	Ethanol	C_2H_6O	1367.3	
169	1-Propanol	C_3H_8O	2021	
170	2-Propanol	C_3H_8O	2005.8	
171	1-Hexanol	$C_6H_{14}O$	3983.8	
172	1-Heptanol	$C_7H_{16}O$	4637.6	
173	Ethan-1,2-diol	$C_2H_6O_2$	1179.5	
174	Propan-1,2,3-triol	$C_3H_8O_3$	1655.2	
175	2-Methylpropan-2-ol	$C_4H_{10}O$	2643.8	
176	Cyclohexanol	$C_6H_{12}O$	3737	
177	Methanal	CH_2O	570.6	
178	Ethanal	C_2H_4O	1167.1	
179	Propanal	C_3H_6O	1820.8	
180	Butanal	C_4H_8O	2476	
181	2-Methylpropanal	C_4H_8O	2468.3	
182	Pentanal	$C_5H_{10}O$	3166	
183	Benzaldehyde	C_7H_6O	3525.1	
184	2-Propanone	C_3H_6O	1816.5	
185	2-Butanone	C_4H_8O	2441.5	
186	3-Methylbutanone	$C_5H_{10}O$	3097	
187	Cyclohexanone	$C_6H_{10}O$	3519.3	
188	Phenylethanone	C_8H_8O	4148.7	
189	Methyl methanoate	$C_2H_4O_2$	972.6	

Table 2. *Cont.*

Sr. No.	Compound Name	Compound Formula	Enthalpy of Combustion (Kcal/mol)	References
190	Cyclopropane	C_3H_6	2091.4	
191	Cyclobutane	C_4H_8	2720.9	
192	Cycloheptane	C_7H_{14}	4598.4	
193	Cyclooctane	C_8H_{16}	5266.7	
194	Cyclononane	C_9H_{18}	5932.5	
195	Styrene	C_8H_8	4395	
196	Acetaldehyde	C_2H_4O	1167	[36]
197	Benzaldehyde	C_7H_6O	843.2	
198	Octaldehyde	$C_8H_{16}O$	1218.9	
199	Ethanedial	$C_2H_2O_2$	205.76	
200	pyrene	$C_{16}H_{10}$	1873.83	[37]
201	1,2-benzanthracene	$C_{18}H_{12}$	2144	
202	perylene	$C_{20}H_{12}$	2334.6	
203	methyl formate	$C_2H_4O_2$	234.1	
204	Heptanal	$C_7H_{14}O$	1062.2	

Once the dataset had been built, the variables were used as inputs to the ANN were calculated. The procedure for the calculation of 11 variables for specific fuels/chemicals, as applied to a few examples, is available in our previous publications [15,16]. After defining all compounds and mixtures, all the definitions and the corresponding enthalpies were imported to MATLAB to yield a neural network with 14 input layers, 26 hidden layers, and 1 output layer. Finally, to obtain the ANN model for predicting the enthalpy of combustion, the model needed to be trained to study and evaluate the effects and the relationships between each of these variables. Some of these effects and relationship are presented in this study.

4. Results and Discussion

The data used for developing the model was obtained from the literature and imported into MATLAB. The impact of the functional groups on the enthalpy of combustion was evaluated by means of various plots. Figures 2–5 show that the enthalpy of combustion increases with an increase in the weight percentage of the paraffinic CH_2 groups present in various chemical classes of the fuels in the dataset. These groups represent the linearity of the hydrocarbon molecule and have been shown to have a significant impact on a number of combustion properties, such as the antiknock rating, ignition quality, flash point, etc.

However, increasing the weight percentage of olefins, alcohols, ketones, and aldehydes results in decreased enthalpy of combustion (see Figures 6–9). However, these figures need to be considered carefully as an increase in the weight percentage of olefins is the result of increasing the CH_2 percentage. Overall, increasing the molecular weight of a compound or a surrogate leads to the increased enthalpy of combustion, as shown in Figures 10–17. Molecular weight has a significant impact on the physical properties of pure compounds and blends and is known to influence properties, including viscosity, density, and surface tension, and also phenomena, such as heating, vaporization, droplet formation, etc. Figure 18 shows the effect of the branching index on the enthalpy of combustion for all of the collected data. It can be clearly observed that, as the branching index increases, the enthalpy of combustion increases for all classes of compounds in the data. The branching index denotes the linearity/nonlinearity of a compound by considering the carbon framework of the compound. Inclusion of the branching index as an input feature has shown to reduce the error in prediction in a large number of studies.

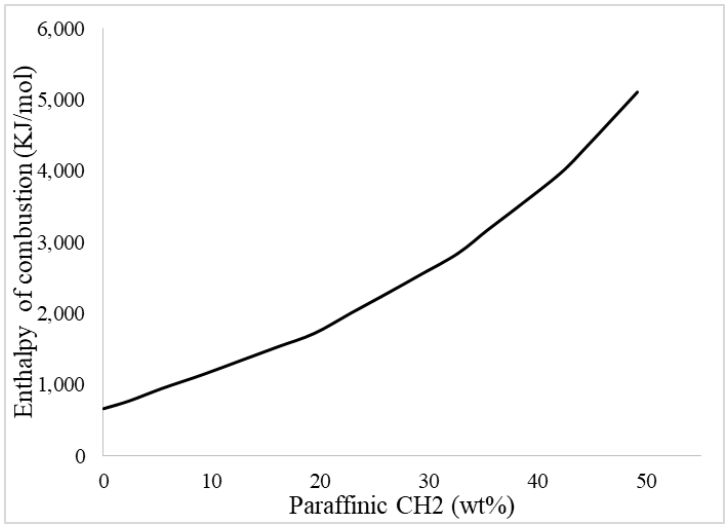

Figure 2. The effect of weight percentage of CH2 on enthalpy of combustion for iso-paraffins.

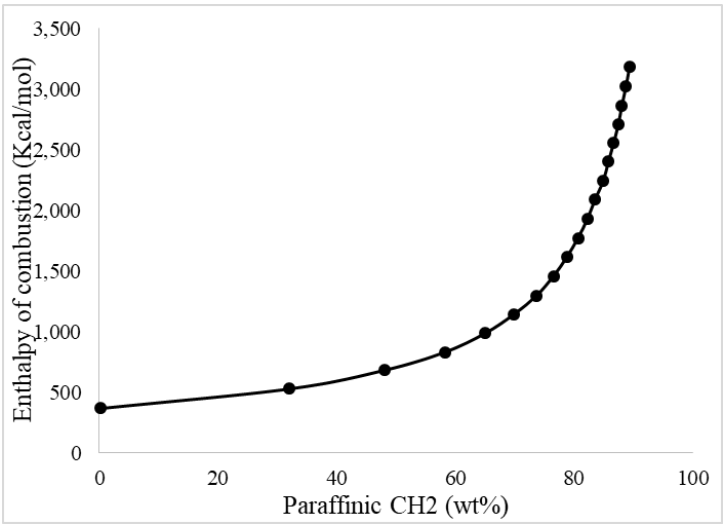

Figure 3. The effect of weight percentage of CH2 on enthalpy of combustion for n-paraffins.

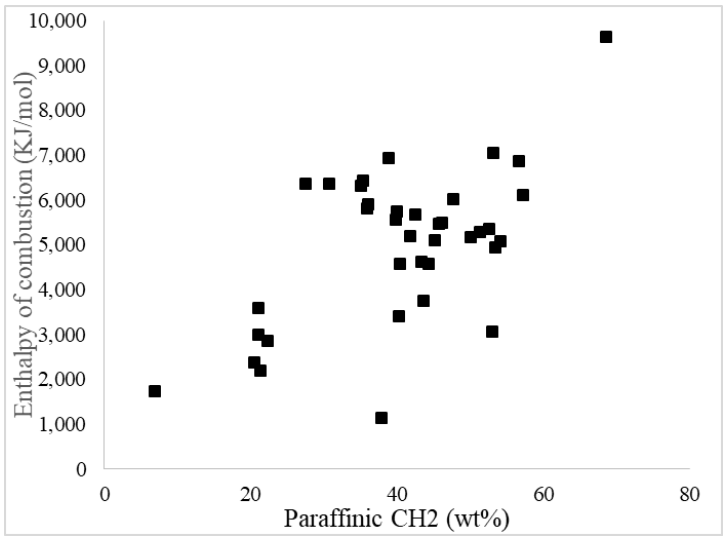

Figure 4. The effect of weight percentage of CH2 on enthalpy of combustion for blends.

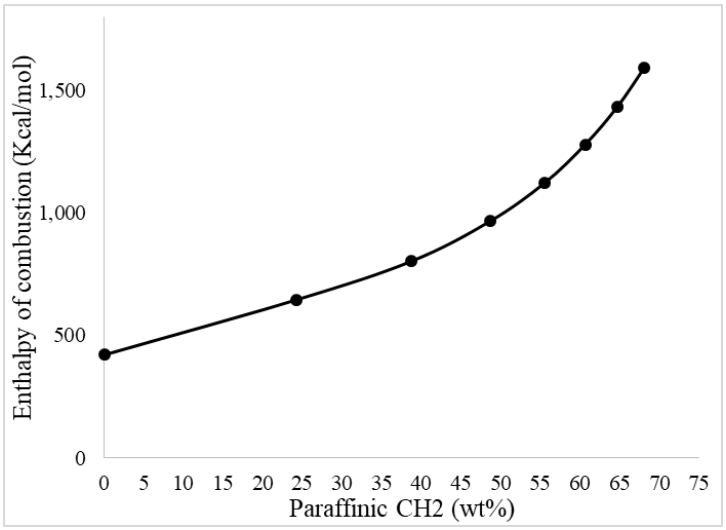

Figure 5. The effect of weight percentage of CH2 on enthalpy of combustion for olefins.

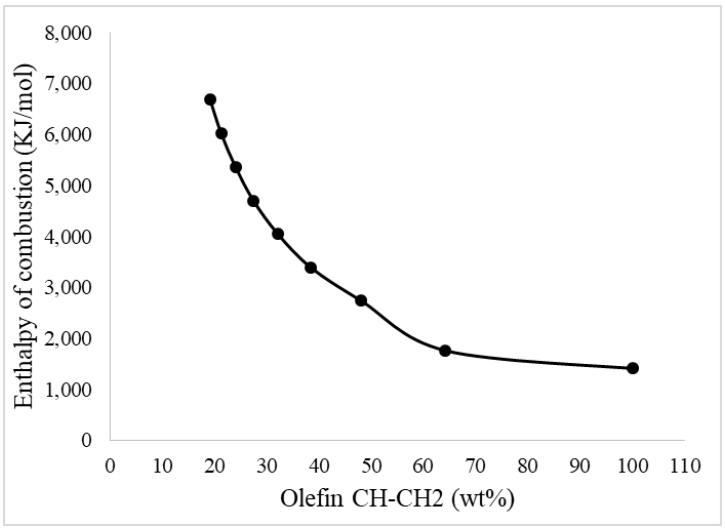

Figure 6. The effect of weight percentage of CH-CH2 on enthalpy of combustion for olefins.

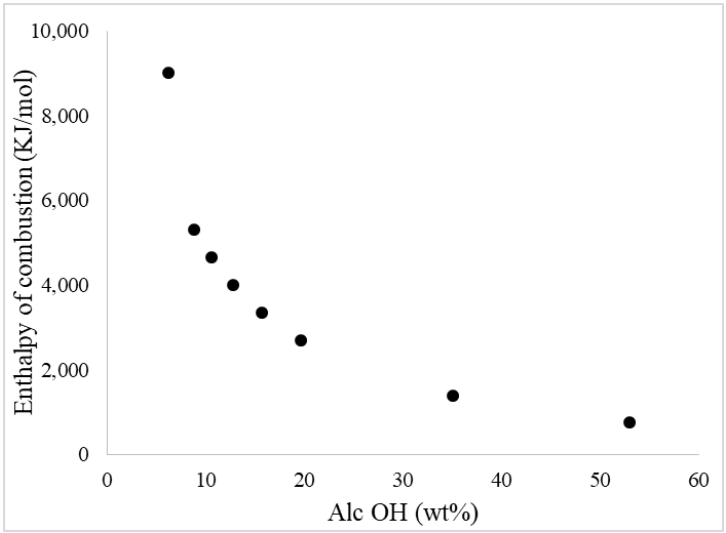

Figure 7. The effect of weight percentage of OH on enthalpy of combustion for alcohols.

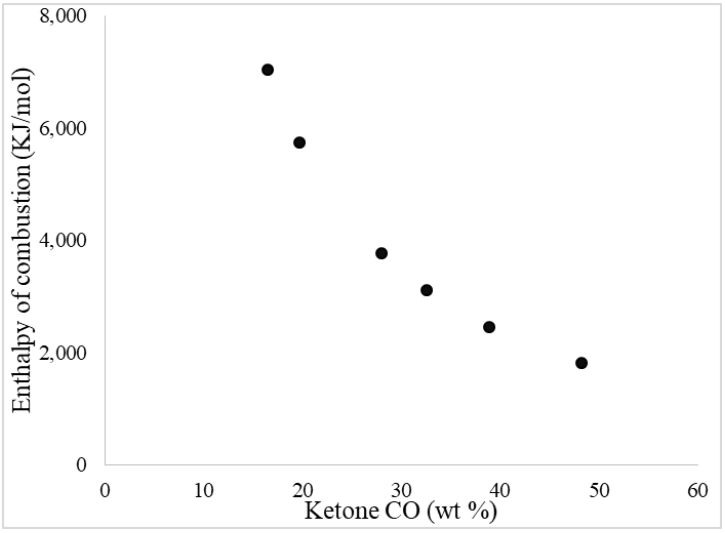

Figure 8. The effect of weight percentage of CO on enthalpy of combustion for ketones.

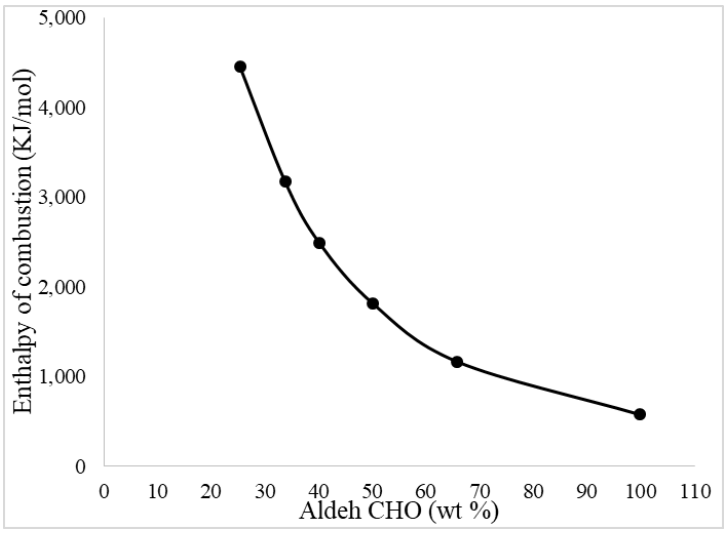

Figure 9. The effect of weight percentage of CHO on enthalpy of combustion for aldehydes.

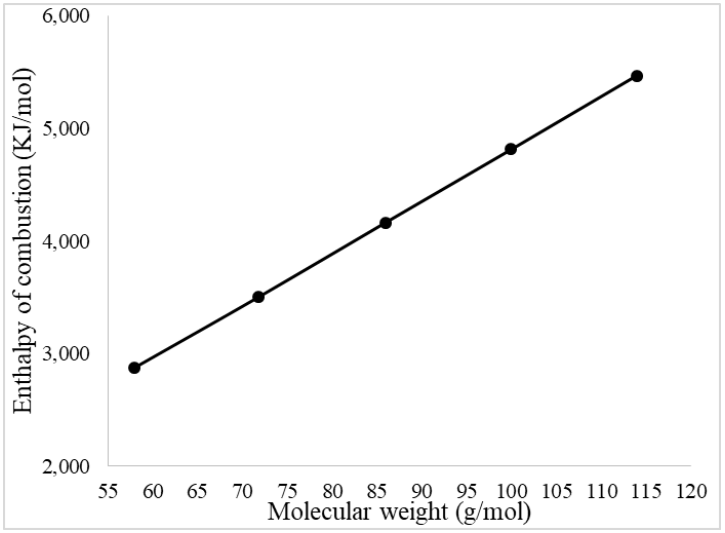

Figure 10. The effect of molecular weight of iso-paraffins on enthalpy of combustion.

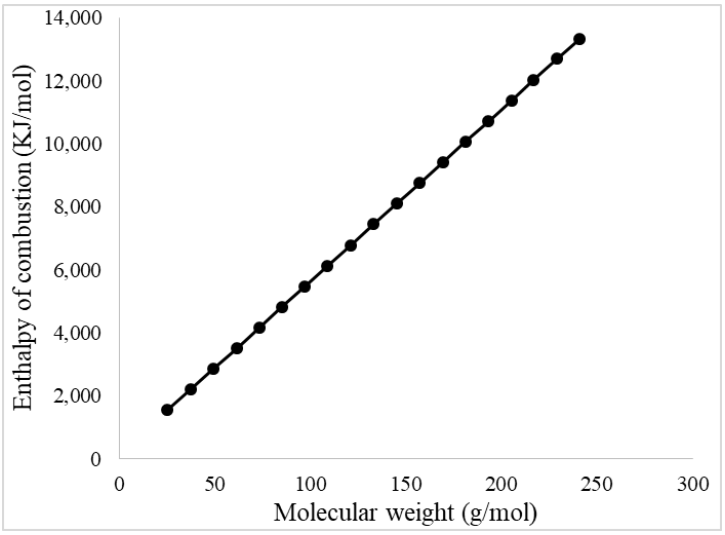

Figure 11. The effect of molecular weight of n-paraffins on enthalpy of combustion.

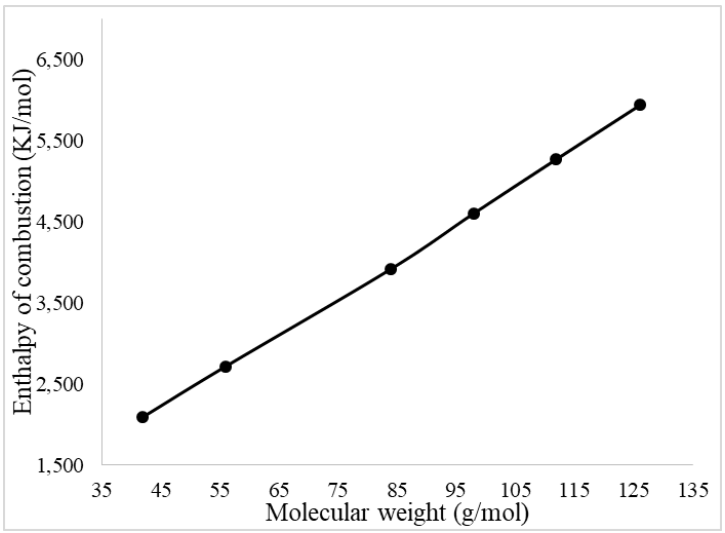

Figure 12. The effect of molecular weight of naphthenes on enthalpy of combustion.

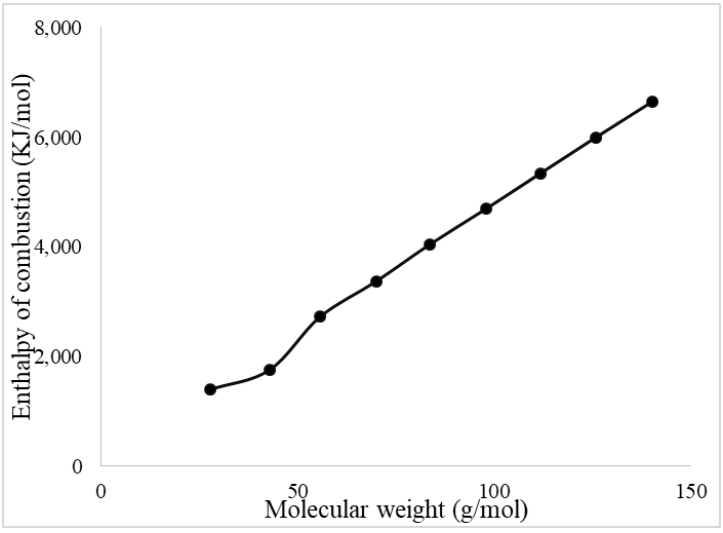

Figure 13. The effect of molecular weight of olefins on enthalpy of combustion.

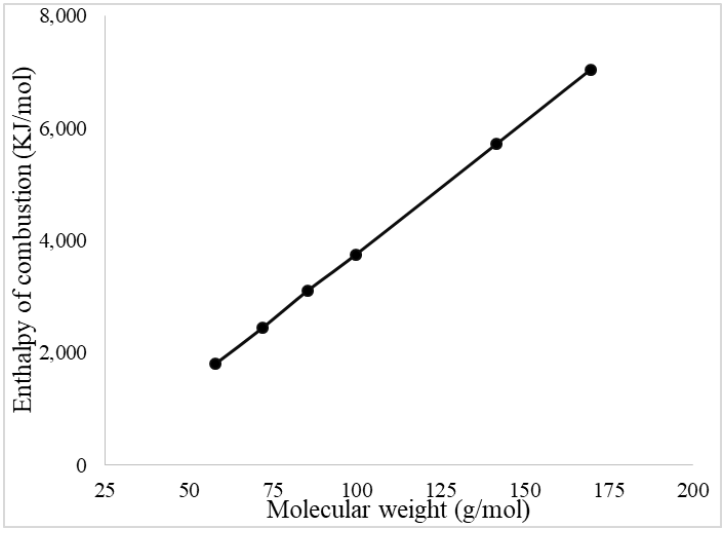

Figure 14. The effect of molecular weight of ketones on enthalpy of combustion.

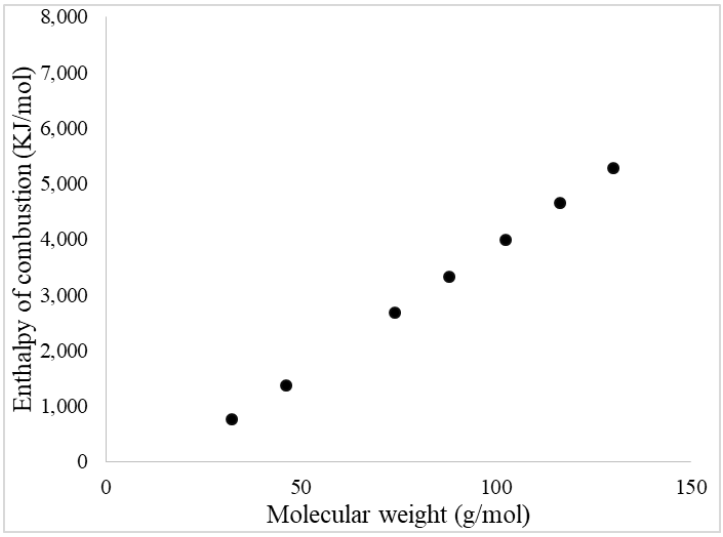

Figure 15. The effect of molecular weight of alcohols on enthalpy of combustion.

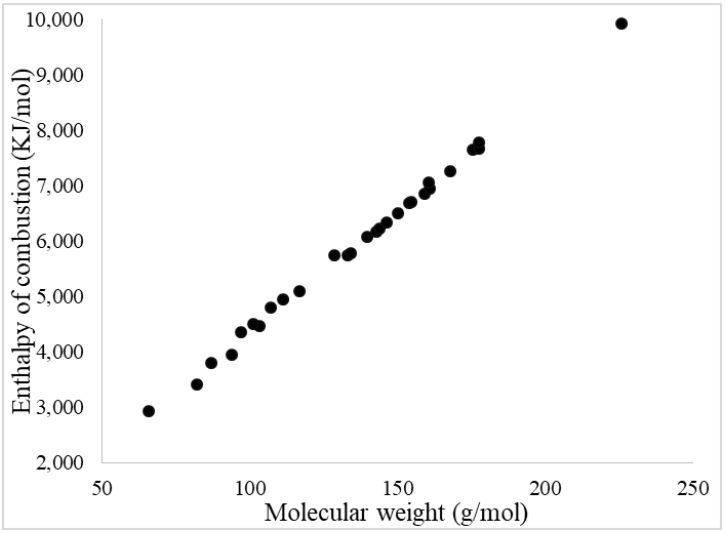

Figure 16. The effect of molecular weight of blends on enthalpy of combustion.

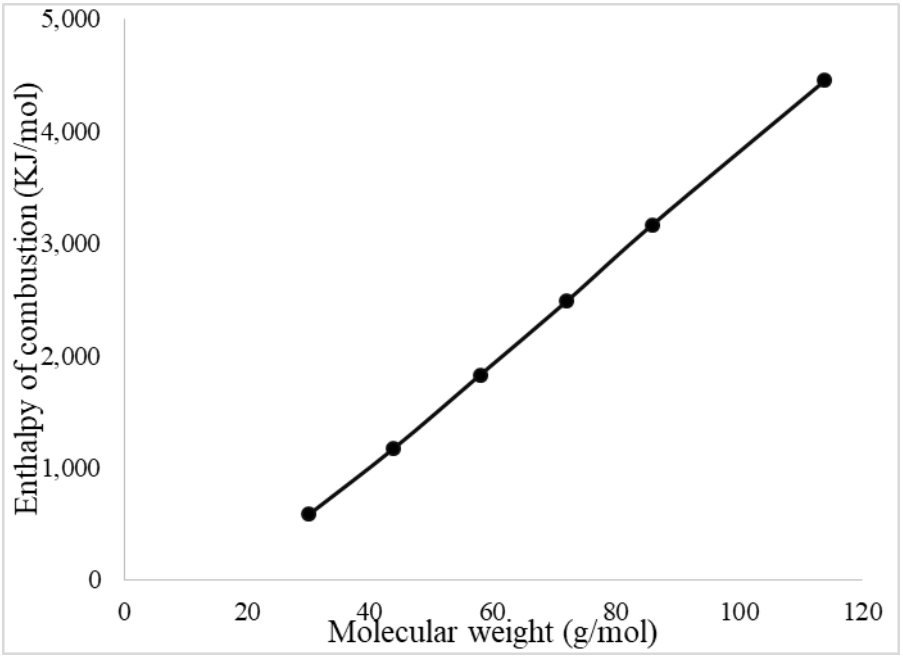

Figure 17. The effect of molecular weight of aldehydes on enthalpy of combustion.

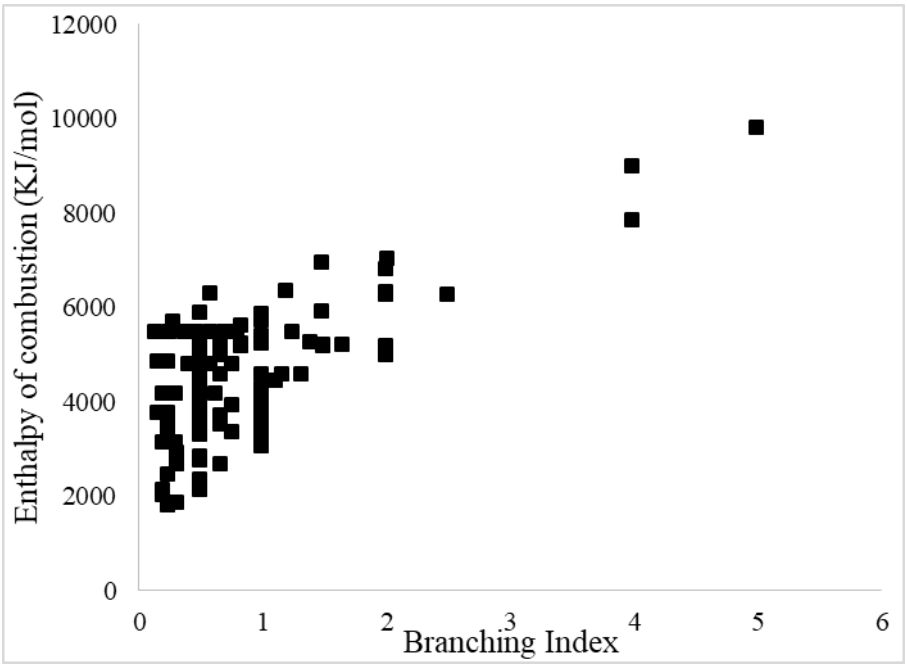

Figure 18. The effect of branching index on enthalpy of combustion for all collected data.

Subsequently, a neural network model was created and trained in MATLAB, resulting in an overall accuracy of 96.3% (see Figure 19). A regression coefficient of 0.959 was obtained when the developed model was applied to the training data, indicating that the model was able to succeed in learning the impact of the input features on the target (i.e., the enthalpy of combustion). The model was validated with approximately 15% of the dataset and yielded a regression coefficient of 0.97. The final testing of the ANN code was performed using a test set that was randomly selected by the software. The measured and predicted enthalpy of combustion values for the 40 compounds of the test set are shown in Table 3. The average percentage error obtained was 4.2%, which is near the range of experimental error.

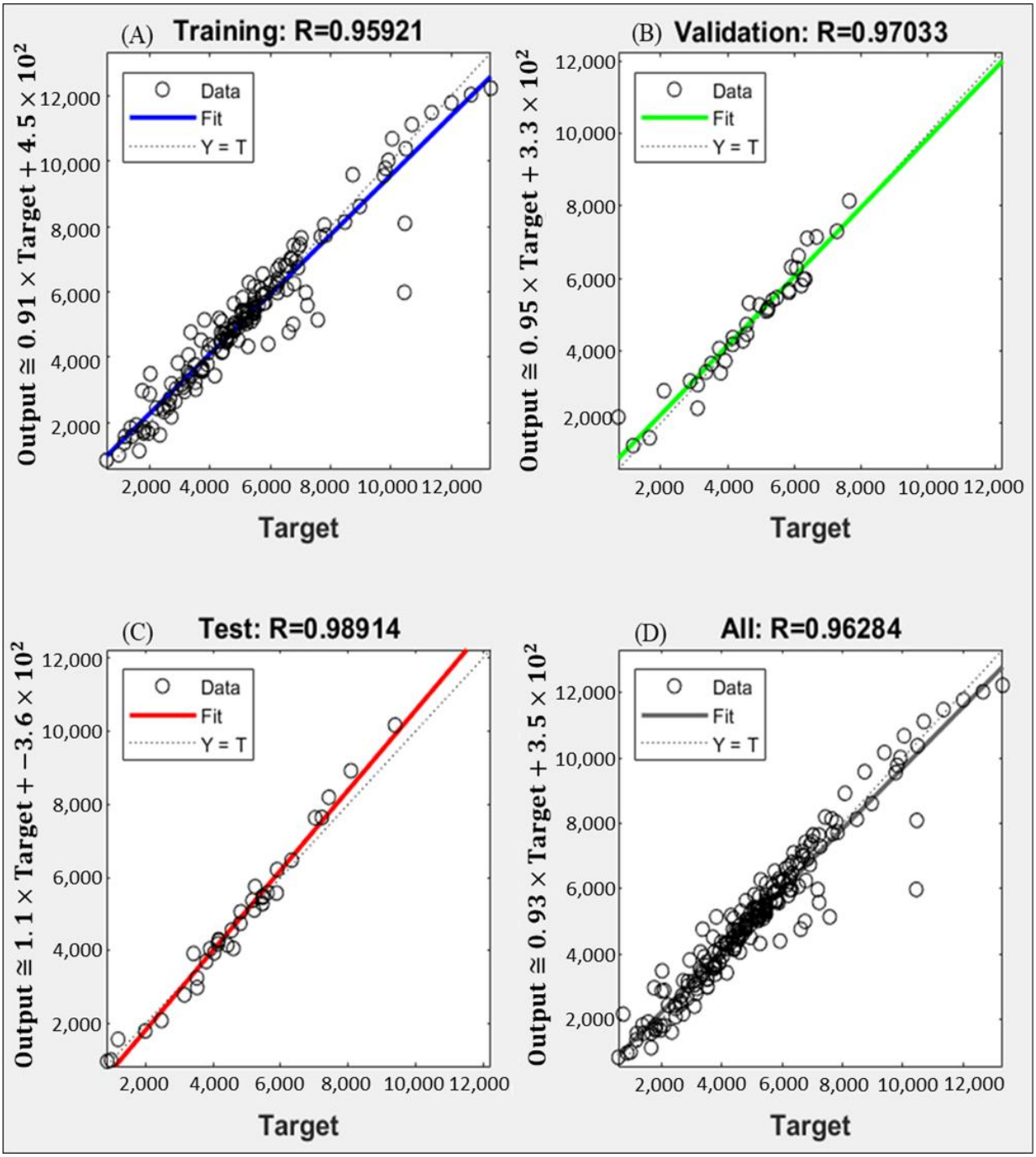

Figure 19. The best obtained result of training the dataset in a neural network.

Table 3. Comparison between the measured enthalpies and the predicted ones.

Sr. No.	Compound Name	Measured/Obtained Enthalpy of Combustion (KJ/mol)	Predicted Enthalpy of Combustion (KJ/mol)	Error (%)
1	2-Methylhexane	4811.5	4819.7	0.2
2	2,2,3-Trimethylpentane	5463.6	5285.9	3.3
3	n-1-Decene	6660.7	7139.8	7.2
4	Propylbenzene	5214.9	5187	0.5
5	1-Methylcyclopentene	3747.6	4056.3	8.2
6	Diphenylstyrene	10,493.5	10,378	1.1

Table 3. *Cont.*

Sr. No.	Compound Name	Measured/Obtained Enthalpy of Combustion (KJ/mol)	Predicted Enthalpy of Combustion (KJ/mol)	Error (%)
7	Heptanal	4444.2	4727.3	6.4
8	Phenol	3064.3	3164.8	3.3
9	Glycerol	1661.5	1587.7	4.4
10	Phenetole	4423.1	4150.6	6.2
11	Pinacolyl alcohol	3925.2	3715.4	5.3
12	Methyl methanoate	972.6	1003.5	3.2
13	Ethanedial	860.9	941.3	9.3
14	Sr#2	6937.1	7359.7	6.1
15	Sr#3	6054.9	6282.3	3.8
16	Sr#4	5755.7	5913	2.7
17	Sr#7	6173.8	6128.9	0.7
18	Sr#8	6205.3	5798.3	6.6
19	Sr#9	6241.7	6388.5	2.4
20	Sr#10	6245.4	6225.6	0.3
21	Sr#11	6671	7016.6	5.2
22	Sr#12	6715.9	6989.8	4.1
23	Sr#13	4950.2	5258.2	6.2
24	Sr#14	3930.1	4128.6	5.1
25	Sr#15	4455.3	4271.8	4.1
26	Sr#16	6550	6076.1	7.2
27	Sr#20	4520	4739.6	4.9
28	Sr#22	4347.7	4471.2	2.8
29	Sr#23	3793.2	3704.6	2.3
30	Sr#25	6334.2	6811.6	7.5
31	Sr#26	6493.8	6804.7	4.8
32	Sr#27	6843.3	6916.7	1.1
33	Sr#28	7795.1	8041.5	3.2
34	Sr#29	7640.7	8319.1	8.9
35	Sr#30	7678.7	7683.5	0.1
36	Sr#31	7033.3	7647.5	8.7
37	Sr#32	5778.1	5646.1	2.3
38	Sr#33	7268.4	7297.5	0.4
39	Sr#34	7223.8	7643.7	5.8
40	Sr#36	9921.4	10,002	0.8

5. Conclusions

This study presents an ANN model with 14 input layers, 26 hidden layers, and 1 output layer to predict the enthalpy of combustion of various oxygenated fuels. The ANN model was built in the MATLAB environment, and it used a detailed dataset of enthalpy of combustion values from the literature. The model was trained, validated, and tested using enthalpy of combustion data for various compounds and fuel surrogates, including numerous chemical classes: paraffins, olefins, naphthenes, aromatics, alcohols, ethers, ketones, and aldehydes. The influence of various functional groups on the enthalpy of combustion has been illustrated graphically and discussed. The procedure for the development of the model has been explained in detail. The overall precision of the developed ANN model in projecting the enthalpy of combustion was approximately 96.3%, and the average percentage error of the model, when applied against the test set, was 4.2. This value is close to that of the experimental uncertainties observed when measuring the enthalpy of combustion. This supervised machine-learning model can be used to predict the enthalpies of pure compounds and real petroleum fuels.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/pr10112384/s1, Table S1. Enthalpy of combustion for surrogates Edwards & Maurice, 2001 [17], Table S2. Enthalpy of combustion for surrogates Huber et al. (2009) [18], Table S3. Enthalpy of combustion for surrogates Shrestha (2014) [19], Table S4. Enthalpy of combustion for surrogates Kalghatgi et al. (2011) [20], Table S5. Enthalpy of combustion for surrogates Huber et al. (2010) [21], Table S6. Enthalpy of combustion for surrogates Eddings et al. (2005) [22], Table S7. Enthalpy of combustion for surrogates Naik et al. (2010) [23], Table S8. Enthalpy of combustion for surrogates Grubinger et al. (2021) [24], Table S9. Enthalpy of combustion for surrogates Xu et al. (2015) [25], Table S10. Enthalpy of combustion for surrogates Grubinger et al. (2021) [24].

Author Contributions: Conceptualization, A.G.A.J. and A.A.-M.; methodology, A.G.A.J. and A.B.S.A.; software, A.A.-M. and U.A.; validation, A.G.A.J., A.A.-M. and A.B.S.A.; formal analysis, N.A. and U.Z.; investigation, A.A.-M.; resources, A.G.A.J.; data curation, U.Z. and U.A.; writing—original draft preparation, A.A.-M. and A.G.A.J.; writing—review and editing, N.A. and A.B.S.A.; visualization, N.A. and U.Z.; supervision, A.G.A.J. and U.A.; project administration, A.G.A.J. and A.B.S.A.; funding acquisition, A.G.A.J. All authors have read and agreed to the published version of the manuscript.

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