CHEMICAL ENGINEERING TRANSACTIONS
VOL. 97, 2022
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Jiří Jaromír Klemeš

ISBN 978-88-95608-96-9; **ISSN** 2283-9216
DOI: 10.3303/CET2297061

Design of Water in Diesel Emulsion Fuel using Computer-Aided Approach

Shah Aznie Ariffin Kashinath, Nor Alafiza Yunus*, Haslenda Hashim

Process Systems Engineering Centre (PROSPECT), Research Institute for Sustainable Environment, School of Chemical and Energy Engineering, Universiti Teknologi Malaysia (UTM), 81310 UTM Johor Bahru, Johor, Malaysia.
alafiza@utm.my

The diesel engine is the main source of exhaust pollutants, mainly nitrogen oxides (NOx) and particulate matter. Water in diesel emulsion (WIDE) is the best and most successful alternative fuel strategy to reduce emissions without modifying the engine. Previous research has used an experimental technique to determine fuel formulation, stability, and environmental impact. Due to the limited number of studies that can be conducted, it is difficult to determine the best formulation via trial and error. This work aims to develop a systematic methodology for the design of WIDE fuel formulations using computer-aided product design. Chemical databases and property model libraries for pure compounds and mixtures for fuel attributes were created explicitly for this study. This investigation consists of four steps. The first step defines the problem by identifying product properties and needs and translating them into physico-chemical parameters as target properties. The second step involves creating databases and property model libraries. A database for nonionic surfactants is created. The property models required for the target properties are retrieved from the property model library at this stage. Screening possible surfactants to be used as input for step 4 is the next step. The last phase is to create a possible WIDE fuel formulation that meets the required parameters. An economic evaluation of the possible formulation is made by comparing the WIDE fuel prices of different surfactants with SPAN 80 as a reference. As a result, six potential surfactants with 48 potential WIDE fuel formulations with water composition from 2% to 11%, diesel from 80.7% to 92.9%, surfactant from 0.1% to 0.46% and additive from 0.1 % to 1% proposed as potential formulations. All the formulations meet the desired parameters set in step 1. Using a computer-aided approach, two surfactants, diethylene glycol monododecyl ether and propylene glycol stearate, have promising potential new surfactants to explore because of the properties and lower price of up to 72.7% compared to SPAN 80. WIDE fuel can be presented as an alternative fuel for diesel engines due to its formulation.

1. Introduction

Diesel fuel is a fossil fuel used in compression ignition or diesel engines. The exhaust emission from the diesel engine emits a more significant amount of greenhouse gas emissions, especially nitrogen oxides (NOx) and particulate matter (PM), leading to climate change. The best solution to reduce both emissions simultaneously is using water in diesel emulsion (WIDE) as a fuel (Ithnin et al., 2015). According to (Guzman et al., 2015), WIDE fuel can reduce 10 % and 40 % of particulate matter and NO_x simultaneously without modification to the engine. Most of the previous studies used an experimental method to formulate WiDE fuel. Many conditions must be considered to formulate high-quality WiDE, such as types of surfactants, fuel stability, water content and properties of emulsion fuel (Badran et al., 2011). The experimental works' limitations are limited to a few formulation factors for WiDE fuel. In addition, this method is time consuming and expensive because it requires testing a large number of samples experimentally. In order to efficiently design the formulation of WIDE fuel, a systematic methodology is needed. Computer-aided methodologies are widely used to design formulated products such as paint, insect-repellent lotion (Conte et al., 2011), gasoline (Yunus et al., 2014), and emulsion-based chemical products (Michele et al., 2014). This study aims to design the formulation of WIDE fuel using a computer-aided approach.

Paper Received: 11 August 2022; Revised: 26 September 2022; Accepted: 6 October 2022
Please cite this article as: Ariffin Kashinath S.A., Yunus N.A., Hashim H., 2022, Design of Water in Diesel Emulsion Fuel using Computer-Aided Approach, Chemical Engineering Transactions, 97, 361-366 DOI:10.3303/CET2297061

2. Methodology

The methodology for formulating WIDE fuel in this case study was adopted from Yunus et al. (2014). There are four steps in the methodology for formulation of WIDE fuel, as shown in Figure 1. A detailed explanation for each step is described in each section.

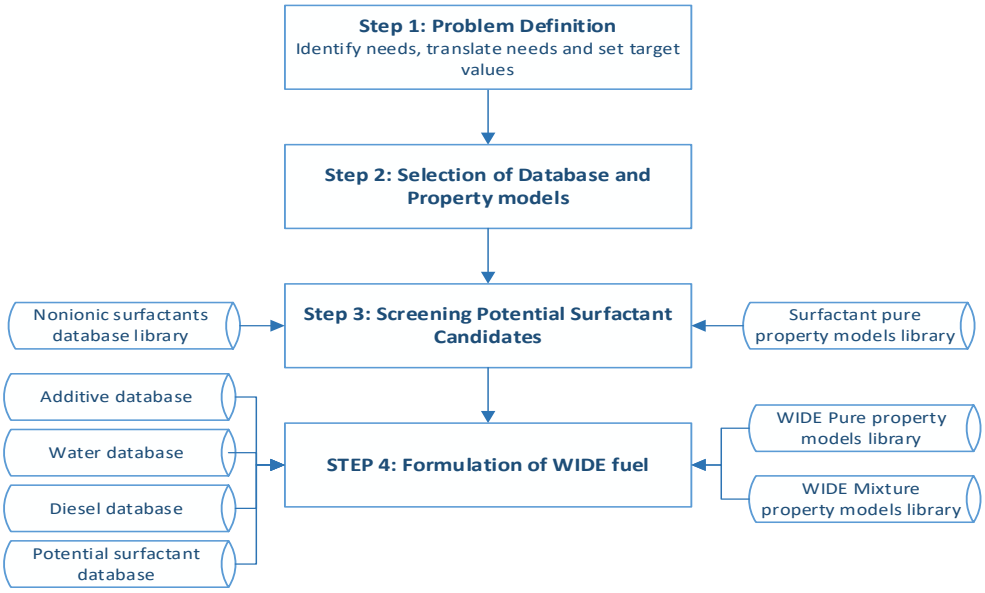

Figure 1: Work-flow for designing water in diesel emulsion fuel

2.1 Step 1: Problem Definition

Designing the WIDE fuel formulation is crucial to understanding the impact of fuel properties on the engine process. For example, to fulfil the optimum operation engine criteria, it is required to have a short ignition delay, which can be achieved by using diesel fuel with high ignition quality or a high value of cetane number (Badran et al., 2011). It also needs to consider the stability of emulsion with suitable surfactant (Hagos et al., 2011). It is crucial to transform user needs into physical properties known as target properties. The target properties' values or boundaries are based on literature or references. Based on the knowledge base, the problem's needs are defined as designing a suitable chemical as an emulsifier for water in diesel emulsion fuel and emulsion properties that suit as potential diesel fuel. The needs, target properties, and boundaries of each property for surfactant and water in diesel emulsion were listed in Tables 1 and 2.

Table 1: Needs and target boundaries of properties of surfactant

Needs	Target Properties	Lower bound	Upper bound	Unit
Good Affinity	Hydrophilic Lipophilic Balance (HLB)	3	6	-
Stability	Critical Micelle Concentration (CMC)	3.393	6.431	mN/m
	Cloud Point (CP)	-15	-	°C
Weaken the surface tension	Surface Tension (ST)	32.8	57.0	N/m

Table 2: Needs and target boundaries of properties of water in diesel emulsion

Needs	Target properties	Lower bound	Upper bound	Unit
Engine efficiency	Heating value (HV)	30	-	MJ/kg
High ignition quality	Cetane number (CN)	40	-	-
Engine performance	Kinematic viscosity	0.2	2	m^2s^{-1}
Better fuel consumption	Density	700	1100	kg/m^3
Reduce exhaust emission	Distillation temperature (DT)	300	-	°C

2.2 Step 2: Selection of database and property models

The database is essential to determine the best surfactant to satisfy the defined needs in Step 1. The researcher can develop a new database, known as a user-defined database, or use the existing chemical databases

developed, such as the CAPEC, Dippr, and Kunifac, available in Integrated Computer-Aided System (ICAS) software. The database for diesel, water, and additive is shown in Table 3. Malaysia's low-grade diesel fuel (D2) diesel properties are collected from Ithnin et al. (2015). A new database of nonionic surfactants consisting of 57 chemicals was developed. The values of the properties are collected from the literature or predicted using the property model in the property model libraries. The chemicals' prices are collected from the internet.

Table 3: The database of diesel, water and additive for the formulation of WIDE fuel

No	Chemical	FM	ρ(kg/m^3)	ln υ(m^{2}s^{-1})	CN	HV(MJ/kg)	T95(°C)	MW(g/mol)	Price (RM/L)
1	Diesel	-	854.7	4.64	54.6	45.28	368	-	2.15
2	Water	H_2O	1024.12	0.664	-	2.254	100	18	12
3	Diethyl ether	$C_4H_{10}O$	713	3.6	125	33.6	34.6	74.12	619

Two property model libraries were developed: the pure property model (consists of surfactant and fuel pure compound models) and the mixture fuel property model. The property models are collected from the literature or developed to improve the efficiency of the prediction. These models are used if the property's value is unavailable in the literature. Surfactant property models predict the target properties surfactant database, while the fuel property models are used to predict the value of the target properties for fuel properties. The mixture property models are the models that will predict the value of the property for the WIDE fuel emulsion. Mixture property model libraries were retrieved to formulate WIDE fuel emulsion in Step 4. Tables 4 and 5 show the property model libraries for pure property for surfactant and fuel.

Table 4: The pure property model library for surfactant

No	Property	Property models	Equation	Reference
1	CMC	GC-method	$-\log(CMC)_{pred} = \sum_i N_i C_i + \sum_j M_j D_j + \sum_k O_k E_k$ (1)	Michele et al. (2014)
2	CP	GC-method	$CP^2 = \sum_i N_i C_i + \sum_j M_j D_j + \sum_k O_k E_k$ (2)	Michele et al. (2014)
3	ST	GC-method	$\mathrm{F}(\sigma) = \sum_i N_i C_i + \mathrm{w}\sum_j M_j D_j + z\sum_k O_k E_k$ (3)	Conte et al. (2008)
4	HLB	GC-method	$HLB = 7 + \sum(hydrophilic\ group\ members) + \sum(lipophilic\ group\ members)$ (4)	Guo et al. (2006)

Table 5: The pure property model library for fuel

No	Property	Property models	Equation	Reference
1	Viscosity	GC-method	$\mathrm{F}(\sigma) = \sum_i N_i C_i + \mathrm{w}\sum_j M_j D_j + z\sum_k O_k E_k$ (5)	Conte et al. (2008)
2	CN	GC-method	$\mathrm{CN} = CN_o + \sum_i N_i C_i + \sum_j M_j D_j + \sum_k O_k E_k$ (6)	Kashinath et al. (2020)
3	HV	GC-method	$\mathrm{HV} = HV_o + \sum_i N_i C_i + \sum_j M_j D_j + \sum_k O_k E_k$ (7)	Yunus et al. (2017)

The mixture property model follows the linear mixing rule for all the target properties listed in Table 2 using Eq(8), where the mixture property ξ_{mix} determined from the pure property $\xi_i$of and the mole fraction, x_i of the compounds in the mixture.

$$\xi_{mix} = \sum_i^n x_i \xi_i \quad (8)$$

2.3 Step 3: Screening potential surfactant candidates

In this step, the method is adopted from Kashinath et al. (2018) where four steps are involved in designing surfactant as an emulsifier for WIDE fuel. The database of surfactants is screened manually by considering HLB, cloud point, CMC and surface tension as target properties. SPAN 80 was used as a reference because it is the common surfactant used in WIDE fuel (Noor El-Din et al., 2013). The chemical will be eliminated if the value exceeds the target boundaries. Six surfactant candidates had fulfilled the target boundaries range of the target properties and were listed as potential surfactants in Table 5. The proposed surfactants have the potential to form a stable emulsion. According to Vellaiyan and Amirthagadeswaran (2016), a Low HLB value makes a stable water-in-oil emulsion, whereas a high HLB tends to make a stable oil-in-water emulsion.

Table 5: The potential surfactants with the target properties for formulation of WIDE fuel

No	Chemical	Label	FM	HV (MJ/kg)	ln υ (m^2s^{-1})	O_2 (%)	Density (kg/m^3)	CN	DT (°C)	MW (g/mol)	Price (RM/L)
1	Sorbitan Monooleate	S1	$C_{24}H_{44}O_6$	0.03	4.10	22.4	994	41.48	300	428.6	692
2	Diethylene glycol monododecyl ether	S2	$C_{16}H_{34}O_4$	0.04	3.41	23.32	989	77.25	371	274.4	365
3	POE(2) stearyl ether	S3	$C_{22}H_{46}O_3$	0.04	4.61	13.39	900	106.52	455.7	358.6	1843.17
4	POE(2) oleyl ether	S4	$C_{22}H_{44}O_3$	0.04	4.35	13.46	900	89.19	484.2	356.6	724/100mg
5	Propylene glycol myristate	S5	$C_{17}H_{34}O_3$	0.04	3.10	33.51	900	70.11	392.2	286.5	N/A
6	Propylene glycol stearate	S6	$C_{21}H_{42}O_3$	0.04	3.79	14.01	900	89.63	447.7	342.6	48.63

2.4 Step 4: Formulation of WIDE fuel

The formulation issue is resolved with the Mixed Integer Linear Programming (MILP) model and a decomposition approach. This process seeks to formulate the best WIDE fuel with the desired target attributes serving as design constraints. A WIDE fuel formulation comprises diesel, water, surfactants, and an additive with particular (derived/target) qualities. The mixture is specifically designed for a purpose derived in Step 1. The decomposition method will gradually reduce infeasible or redundant candidates through the hierarchy of (property) model-based constraints (Yunus et al., 2014). In this case study, two stages of sub-problem are involved in getting the optimum composition of WIDE fuel, labelled as sub-problem 1 and sub-problem 2. Sub-problem 1 involves a subset of constraints from the original set and consists of the mixture fuel property models (listed in step 2). Sub-problem 2 will solve the objective function of the problem. For this case study, The mixture property model was used to generate the feasible fuel formulation. The objective functions are to minimize and maximize the composition of each component, Eq (9) subject to the linear constraints, Eq (10) representing density, kinematic viscosity,HV, CN and DT to fulfil the target boundaries set in Table 2. MATLAB was employed as a tool to produce the formulation of WIDE fuel.

$$min\ or \max f_{obj}(x) \tag{9}$$

$$s.t \quad \xi_{LB}^{k} \leq \sum_{i}^{n} x_i \xi_i \leq \xi_{UB}^{k} \tag{10}$$

$$\sum_{i}^{n} x_i - 1 = 0 \tag{11}$$

$$0 < \mathrm{x_i} < 1 \tag{12}$$

The results from this section are further analyzed regarding the economic factor by comparing the fuel price to the WIDE fuel with a commonly used surfactant (SPAN80).

3. Results and discussion

A total of 48 potential WIDE fuel formulation is generated and fulfilled all the target boundaries of the physicochemical properties of the target properties set in Step 4. Table 10 shows the results of the formulation of WIDE fuel. All the potential surfactants (S1 to S6) can form a WIDE fuel within the target boundaries. The range of composition of water is from 2 % to 11 %, diesel is 80.7 % to 92.9 %, surfactant is 0.1 % to 0.46 % and additive is 0.1 % to 1 %.

Each property's target boundaries are set to improve diesel engine performance and combustion. For example, the properties values for the potential 48 formulations are listed in Tables 11 to 12. All the predicted values of the properties are within the range set in the target boundaries in Step 1. The property values also show that the formulation generated has good properties value as a fuel. For example, all the target values have a cetane number set with a minimum value of 40. For most formulations, the cetane number is greater than 55, which is very good for the fuel with a cetane number greater than 55. According to Elvers (2007), oil companies and motor manufacturers have studied the effect of fuel properties and composition in the European Program on Emissions, Fuels and Engine Technologies (EPEFE). Cetane numbers with a value of 55 and above can simultaneously reduce the carbon monoxide, hydrocarbon, and particulate matter compared with the fuel with

a CN value is 50. It is shown that using the computer-aided approach, the fuel properties can be designed to achieve the target set for target properties.

Table 10: Composition of water in diesel emulsion fuel

Label	Surfactant	Diesel (wt%)	Water (wt%)	Surfactant (wt%)	Additive (wt%)	Objective function
1A	S1,S2,S3, S4,S5,S6	0.8069	0.0831	0.0100	0.1000	1 (min diesel)
1B		0.9288	0.0512	0.0100	0.0100	2 (max diesel)
1C		0.8510	0.0262	0.0228	0.1000	3 (min water)
1D		0.8733	0.1067	0.0100	0.0100	4 (max water)
1E		0.8228	0.0842	0.0100	0.0830	5 (min surfactant)
1F		0.8752	0.0686	0.0462	0.0100	6 (max surfactant)
1G		0.8773	0.0768	0.0359	0.0100	7 (min additive)
1H		0.8086	0.0562	0.0353	0.1000	8 (max additive)

Table 11: The heating value and kinematic value of WIDE fuel

Label	HV(MJ/kg)						ln υ (m^2s^{-1})					
	S1	S2	S3	S4	S5	S6	S1	S2	S3	S4	S5	S6
1A	40.0	40.0	40.0	40.0	40.0	40.0	1.36	1.35	1.37	1.36	1.35	1.36
1B	42.4	42.4	42.4	42.4	42.4	42.4	1.44	1.44	1.45	1.45	1.43	1.44
1C	41.9	41.9	41.9	41.9	41.9	41.9	1.50	1.49	1.52	1.51	1.48	1.50
1D	40.0	40.0	40.0	40.0	40.0	40.0	1.34	1.33	1.34	1.34	1.33	1.33
1E	40.1	40.1	40.1	40.1	40.1	40.1	1.36	1.36	1.37	1.37	1.35	1.36
1F	40.0	40.0	40.0	40.0	40.0	40.0	1.50	1.47	1.52	1.52	1.46	1.49
1G	40.1	40.1	40.1	40.1	40.1	40.1	1.46	1.44	1.48	1.47	1.43	1.45
1H	40.0	40.0	40.0	40.0	40.0	40.0	1.48	1.45	1.50	1.50	1.44	1.47

Table 12: The values of the cetane number and density of WIDE fuel

Label	Cetane Number						Density (kg/m^3)					
	S1	S2	S3	S4	S5	S6	S1	S2	S3	S4	S5	S6
1A	58.18	58.54	58.83	58.66	58.47	58.66	852.60	851.27	850.12	850.11	849.91	850.07
1B	53.77	54.13	54.42	54.25	54.06	54.25	857.10	855.93	854.86	854.85	854.69	854.82
1C	61.19	62.00	62.67	62.28	61.84	62.29	855.91	853.13	850.65	850.63	850.21	854.46
1D	50.66	51.02	51.31	51.13	50.94	51.14	858.12	856.90	855.76	855.75	855.58	857.48
1E	56.95	57.31	57.60	57.43	57.24	57.43	853.63	852.32	851.17	851.17	850.97	852.94
1F	52.27	53.92	55.27	54.47	53.59	54.49	868.21	863.20	858.16	858.14	857.43	865.64
1G	51.96	53.24	54.29	53.67	52.98	53.68	866.25	861.42	857.46	857.45	856.88	863.36
1H	59.33	60.59	61.62	61.01	60.34	61.03	860.40	856.13	852.16	852.14	851.49	858.19

By comparing fuel costs with various surfactants, all feasible formulations are analyzed. The formulations with the highest surfactant concentration (1F) are chosen for the calculation example. Table 13 displays the cost of WIDE fuel with S1 through S6.

Table 13: The price of WIDE fuel with different surfactants

Surfactant	Diesel (wt%)	Water(wt%)	Surfactant (wt%)	Additive (wt%)	Price (RM/L)
S1(Reference)	0.8752	0.0686	0.0462	0.0100	40.87
S2	0.8752	0.0686	0.0462	0.0100	25.76
S3	0.8752	0.0686	0.0462	0.0100	94.05
S4	0.8752	0.0686	0.0462	0.0100	342,891.40
S5	0.8752	0.0686	0.0462	0.0100	N/A
S6	0.8752	0.0686	0.0462	0.0100	11.14

The prices of WIDE fuel containing the surfactants S2 and S6 are lower than those of S1, which was commonly used in previous research. It demonstrates that the formulation of WIDE fuel can be designed with the optimal

composition using potential surfactants with suitable properties and a lower price using a computer-assisted method.

4. Conclusions

A systematic methodology for formulating WIDE fuel emulsions has been developed. The proposed fuel met the specified property limits with WIDE fuel's optimal and workable formulation. Six potential surfactants for water formation in diesel emulsions were investigated. Consequently, 48 viable candidates for WIDE fuel in the optimal state with a water content ranging from 2 to 11% with six potential surfactants as emulsifiers can be proposed as potential fuels. The economic evaluation is made for the potential WIDE fuel by comparing the fuel price with sorbitan monooleate. WIDE Fuel with Surfactants diethylene glycol monododecyl ether and propylene glycol stearate surfactants have a lower price and can be suggested as potential surfactants for future research. The price of the formulations is lower at 36.98% and 72.7%, respectively, compared to SPAN 80. Further experimental verification and analysis of engine performance and emission factors must be performed on the WIDE fuel candidates shortlisted for further testing. This methodology can be used to design WIDE fuel formulation in future research depending on the databases of surfactants and additives and the property model libraries. This method can be extended for future work by examining and expanding the number of potential surfactant and additive databases and refining the requirements based on the nature of the problem. This method can save money and time due to the high cost of surfactants, and the experimental work can be planned based on the proposed formulation instead of using a random trial and error approach.

Acknowledgements

The authors would like to thank Universiti Teknologi Malaysia and Ministry of Higher Education under the Fundamental Research Grant Scheme (FRGS) number: FRGS/1/2021/TK0/UTM/02/38 for funding this project.

References

Ariffin Kashinath S.A., Hashim H., Yunus N.A., Mustaffa AA, 2018, Design of surfactant for water in diesel Emulsion Fuel for Designing Eco-Friendly Fuel, Chemical Engineering Transactions, 63, 433-438.

Ariffin Kashinath S.A., Hashim H., Mustaffa A.A., Yunus N.A., 2020, Cetane Number Estimation of Pure compound using Group Contribution Method, Chemical Engineering Transactions, 78, 331-336.

Badran O., Emish S., Abu Zaid M., Tayser A., Mohammad A., Mumin A., 2011, Impact of emulsified water/diesel mixture on engine performance and environment, International Journal of Thermal & Environmental Engineering, 3 (1), 1-7.

Conte E., Marstinho A., Matos H. A., Gani R., 2008, Combined group-contribution and atom connectivity index-based methods for estimation of surface tension and viscosity, Industrial & Engineering Chemistry Research, 47(20), 7940–7954.

Conte E., Gani R. and Ng K.M., 2011, design of formulated products: a systematic methodology. AIChE Journal. 57, 2431-2449.

Guo X., Rong Z., Ying X., 2006, calculation of hydrophile–lipophile balance for polyethoxylated surfactants by group contribution method, Journal of Colloid and Interface Science, 298(1), 441–450.

Guzmán M.A., Katherine A.L., Agudelo J.R., 2015, Combustion characteristics, performance and emissions of a diesel engine fuelled with water/diesel emulsions, Chemical Engineering Transactions, 45, 1039-1044.

Hagos F.Y., Aziz A.R.A., Tan I.M., 2011, Water-in-diesel emulsion and its micro-explosion phenomenon-review, 3rd International Conference on Communication Software and Networks, 27th-29th May, Xi'an, China, 314-318.

ICAS v18.0, 2014, CAPEC, Technical University of Denmark, Kongens Lyngby, Denmark.

Ithnin A.M., Ahmad M.A., Bakar M.A.A., Rajoo S., Yahya WJ, 2015, Combustion performance and emission analysis of diesel engine fuelled with water-in-diesel emulsion fuel made from low-grade diesel fuel, Energy Conversion and Management, 90, 375–382.

Michele M., Georgios MK, Gani R., 2014, A comprehensive framework for surfactant selection and design for emulsion based chemical product design, Fluid Phase Equilibria, 362, 288 – 299.

Noor El-Din M.R., Sabrnal H., El-Hamouly M., Marwa H. M., Mishrif R., Ahmad M.R., 2013, Water-in-diesel Fuel Nanoemulsions: Preparation, Stability and Physical Properties, Egyptian Journal of Petroleum, 22, 517-530.

Yunus N.A., Gernaey K.V., Woodley J.M., Gani R., 2014, Design of sustainable blended products using an integrated methodology, Computer Aided Chemical Engineering, 32, 835-840.

Yunus N.A., Zahari NNNNM, 2017, prediction of standard heat of combustion using two-step regression, Chemical Engineering Transactions, 56,1063-106.