PROCESS PARAMETERS OPTIMIZATION OF WATER-WASTE DERIVED BIODIESEL EMULSION PERMUTE AS A SUSTAINABLE AND GREENER ENERGY SOURCE

by

Mahesh GURUSAMY[a*], Muralidharan KANDASAMY[b], and Suresh VELLAIYAN[c]

[a] Department of Mechanical Engineering, JCT College of Engineering and Technology, Coimbatore, Tamilnadu, India
[b] Department of Mechanical Engineering, Sona College of Technology, Salem, Tamilnadu, India
[c] Department of Sustainable Engineering, Saveetha School of Engineering, SIMATS, Chennai, Tamilnadu, India

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The present study aims to optimize the process parameters to formulate a stable water-biodiesel emulsion fuel and permute it as a sustainable and greener source for biofuel application. Biodiesel is derived from waste orange peels and its chemical constituents are characterized. Water emulsion in base fuel is considered to promote energy-and-environmental impacts. As the quality of emulsion fuel depends on the physicochemical properties which are directly influenced by base fuel, water, and surfactant concentrations, a multi-response optimizationol is implemented to derive the optimum levels for process parameters. The optimization result shows that the base diesel blended with 30% orange peel oil, 10% water, and 1% surfactant promotes superior fuel quality, and the water has a maximum influence on fuel quality (54.41%). The emission assessment at peak brake mean-effective indicates that the hydrocarbon, CO, NO_x, and smoke emissions are reduced by 26.9%, 49%, 4.1%, and 17.2% at optimal conditions compared to base diesel, respectively.

Key words*: orange peel oil, fuel characteristics, water emulsion, multi-response optimization, emission assessment*

Introduction

In the present century, fossil fuel consumption is increasing rapidly and its reserve is estimated to empty in another two to three decades [1]. Fossil fuel, especially diesel, has a significant role in the world economy and it is a prime source for transportation, power, and electric vehicle sectors [2]. On the other hand, a millionns of energy resources are wasted by our human and industrial activities without utilizing them in a useful manner. Hence, a much-needed balance between these two critical issues is to be developed by the scientific community to save the environment.

Municipal solid waste, process waste, medical waste, and agricultural waste are the primary sources of energy and are under the umbrella of the latest waste-to-energy technology. The World Energy Council reported that global waste to reach by 6 millionnnes per day by 2025

* Corresponding author, e-mail: drmaheshgurusamy@gmail.com

while considering the current rate of waste formation [3]. The report also states that an increase in the waste-to-energy utility scale is a constructive way to save energy. Out of different feeds, industrial waste dominates and about 31% of energy will be recovered from industrial waste.

Orange peel plays a major role in pharmacy and healthcare industries due to its abundant nutritional value and its contribution is extended to food industries also in a significant manner [4]. The waste orange peel from the food and pharma industry has a rich carbon content, which is an essential requirement to convert them into a renewable energy material [5]. Apart from that, the oil from the orange peel has supplemented oxygen and calorific value along with low flow resistance that could make it a promising alternative energy for engine applications [6].

A thermal/steam distillation process is widely accepted to recover the energy from the citrus peels as the distillation process leads to higher energy yield, and the kinematic viscosity of the fuel is kept low compared to other methods, which are the positive signs for the combustion process [7]. Some interesting studies have been conducted to identify the quality of orange peel oil (OPO) and the reports stated that the fuel properties are in-line with the ASTM standards [6, 8, 9]. However, the study reports conclude that though the OPO serves as an alternative energy source, the NO_x emission from the oxygen-enriched OPO have the foulest effect on environmental health and this issue needs to be addressed stringently.

Generally, the NO_x emission formation is accelerated at a high local combustion temperature. An increase in combustion temperature further increases the tendency of NO_x formation [10]. On the other hand, a drop in the combustion flame temperature leads to a low engine torque [11]. Hence, to balance the NO_x emission formation and engine torque, water emulsion in the base fuel is recommended by eminent researchers in various stages and the same has been proposed for OPO in this study. Since the base diesel (BD), OPO and water are immiscible, an additional agent in the form of surfactant needs to be introduced into the emulsion fuel [12]. Out of different ionic and non-ionic surfactants, non-ionic surfactant with a hydrophilic-lipophilic balance (HLB) value of 7-9 is mostly recommended by many reports as these non-ionic surfactants have a higher emulsifying ability [13-15].

The aforementioned discussions pointed out that the OPO has interesting qualities to meet the energy demand, and the water in OPO along with suitable surfactants has added advantages such as low NO_x emission and better engine performance. However, these parameters have a unique characteristic on overall fuel qualities *i.e.*, the effect of one parameter on the fuel quality differs from others. Hence, it is a much-needed effort to find the optimum level of individual parameters to enhance the overall fuel quality.

The Taguchi method is the best tool for individual response optimization and is not recommended for multi-objective optimization [16]. Since fuel quality depends on the combined effort of key fuel properties, a multi-objective optimizationol will be recommended for fuel quality studies. Out of different multi-objective optimization techniques, grey-relational analysis coupled with the Taguchi method is identified as a suitable tool due to its better accuracy and simplicity compared to others [17-19].

From the previous deliberations, it is identified that the OPO has the potential to meet the energy demand and can be effectively used for engine application by improving its quality. Water emulsion in OPO is a novel attempt to enrich its energy and environmental impact on the diesel engine. However, the emulsion stability period is a key factor in the emulsion fuel domain, and the stability period purely depends on the nature of the surfactant and its concentration. Hence, the present study aims to optimize the process parameters to formulate a stable water-OPO emulsion fuel and permute the derived fuel as a sustainable and greener energy

source for the existing diesel engine application. Additionally, the environmental assessment of test fuel prepared at optimum condition has also been carried out and compared with BD.

Methodology

Energy extraction from OPO and its chemical constituents

The waste orange peels are collected in the local market and dried under normal sunlight. The OPO extraction set-up consists of a steam boiler, distillation chamber, condenser, and collection jar are represented in fig. 1. The dried orange peels reserved in the distillation chamber exposed the OPO during the steam heating process. The steam from the boiler is permitted to pass over the surface of the orange rinds. The hot steam reacted over the surface of the orange peel and break the carbon chain of the orange peel. The fume form of steam and OPO mixture is gathered in the condenser and the OPO is condensed. The low density OPO is floating over the high density water, which is collected separately and heating and filtration processes are executed to remove the impurities.

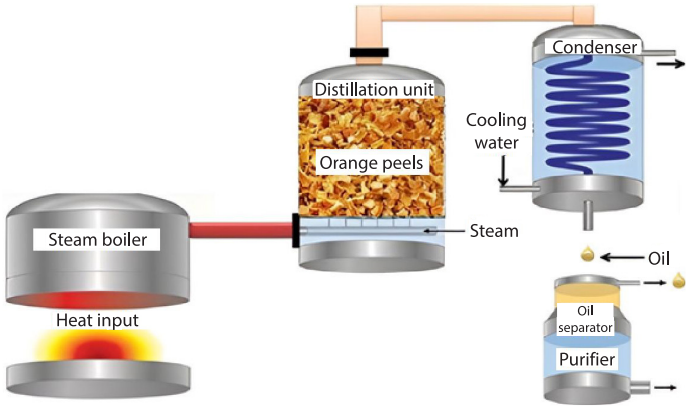

Figure 1. Schematic lay-out of the thermal distillation process to extract OPO

The chemical constituents of OPO have been perceived by gas chromatography-mass spectrometry analysis. The chemical constituent's analysis indicates that the majority of contribution (about 73%) is from 1-methyl-4-prop-1-en-2-ylcyclohexene followed by 1-isopropyl-4-methyl-1,4-cyclohexadiene (about 14%). The remaining constituents such as pinene, myrcene, ocimene, 1,3-dimethyladamantane, trans-α-Bergamotene, trans-α-Bergamotene, and Germacrene are contributed in low percentage volume. The mentioned fatty acid constituents present in the OPO assure that the OPO is a suitable sustainable energy source for the development of biofuel.

Water-OPO emulsion preparation

A two-phase emulsion *i.e.*, a water-in-OPO emulsion is prepared using a mechanical agitator with sorbitan monolaurate surfactant ($C_{18}H_{34}O_6$) with an HLB value of 8.6 (Sigma Aldrich, India). During the emulsion preparation, the mixture of BD and OPO is a constant phase, and the water is a discrete phase. The desired quantity of OPO is initially blended with base fuel and kept in the container. The surfactant and water are slowly added with the constant phase and agitated for about 30 minutes to form a stable emulsion. The schematic lay-out of the water-OPO emulsion preparation set-up is represented in fig. 2.

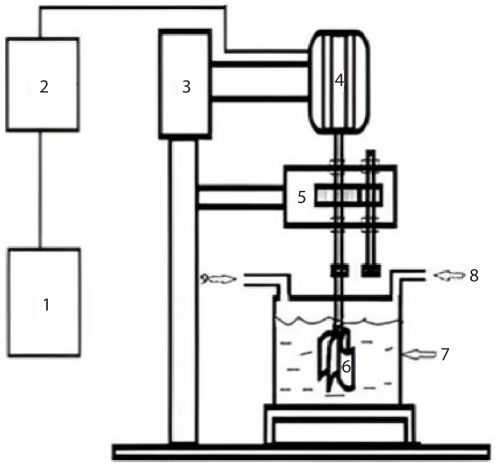

Figure 2. Schematic lay-out of water-OPO emulsion fuel preparation set-up;
1 – power supply,
2 – auto transformer,
3 – base frame, 4 – motor,
5 – speed regulator, 6 – stirrer,
7 – base fuel, 8 – water inlet,
and 9 – surfactant inlet

Properties measurement

The key important fuel properties that directly influence the energy and environmental impact of the engine are density, viscosity, calorific value, stability period, and flashpoint. ASTM standards such as ASTM D1298 (density at 15 °C, hydrometer), ASTM D445 (viscosity at 40 °C, viscometer), ASTM D240 (bomb calorimeter), and ASTM D93 (flashpoint, closed cup apparatus) are followed to measure the previously said physicochemical properties. The stability period was measured by using a laser-assisted photonic circuit which is developed in our previous study [20].

Emulsification process parameters and their levels

The OPO concentration, water concentration, and surfactant concentration are considered in this study to make OPO an alternative source for engine application. Three levels of OPO concentration in base fuel have opted for this study (10%, 20%, and 30%). The OPO level in base fuel is limited to 30% as the higher level of low viscous fuel in the diesel engine exhibits a negative impact on performance and emissions [16]. The second process parameter is a water concentration, which is also having three levels in the base fuel such as 5%, 10%, and 15%. Though the water emulsion has a positive impact on the overall performance of the diesel engine, there is a threshold limit and the majority of studies report that the limit is in-between 5-15% [21-23]. The surfactant concentration also has a vital role in emulsion preparation as the surfactant reduces the surface tension between the continuous phase and dispersion phase to make a stable emulsion [24, 25]. If the emulsion starts to separate during the engine application, it will completely damage the combustion system [26]. However, the high concentration of surfactant in base fuel could resist the flowability and lead to a negative impact [13]. Hence, the surfactant concentration started from 0.5% in emulsion fuel and is restricted to 1.5%. Based on the aforementioned constraints, Taguchi's L_9 orthogonal array is recommended to follow for the present study.

Taguchi-grey relational analysis

Concerning processing parameters and their levels, test fuels are prepared based on the L_9 combination. The fuel properties (output responses) are categorized as *higher-the-better*

and *lower-the-better* based on the consequence of fuel properties during the combustion. The calorific value, stability period, and flashpoint of the fuel are considered *higher-the-better*, and the fuel viscosity and density are considered "lower-the-better". The fuel properties are characterized by applying the equations [16]:

– higher-the-better

$$x_{(i)}k = \frac{y_i(k) - \text{minimum of } y_i(k)}{\text{maximum of } y_i(k) - \text{minimum of } y_i(k)} \tag{1}$$

– lower-the-better

$$x_{(i)}k = \frac{\text{maximum of } y_i(k) - y_i(k)}{\text{maximum of } y_i(\text{k}) - \text{minimum of } y_i(k)} \tag{2}$$

where $x_i(k)$ is a sequence of comparison and $y_i(k)$ – the an original sequence. The smallest and highest value in the original sequence is represented by minimum of $y_i(k)$ and maximum of $y_i(k)$.

The Taguchi method is coupled with the grey relational analysis for collective responses, and the grey-relational coefficient (GRC) is estimated by applying the following equation [16]:

$$\xi i(k) = \frac{\Delta_{\text{minimum}} + \psi\Delta_{\text{maximum}}}{\Delta_{0i}(k) + \psi\Delta_{\text{maximum}}} \tag{3}$$

where Δ_{0i} is the absolute difference, and $\Delta_{\max}$ and $\Delta_{\min}$ are the maximum and minimum values in Δ_{0i}

From the GRC, the overall grey-relational grade (GRG) of the fuel properties is calculated concerning the weightage factor, β. All the properties have been assigned with common weightage, and the GRG and signal-to-noise (S/N) ratios are predicted by applying the following equation [16]:

$$GRG = \sum_{k=1}^{n} \xi_i(k)\beta y_i \ldots, \sum \beta = 1 \tag{4}$$

$$S/N \text{ ratio} = -10\log\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2} \tag{5}$$

Emission test set-up

The emission characteristics of sample fuels prepared at optimum conditions are executed under maximum brake mean effective pressure (BMEP) conditions in a single-cylinder and four-stroke Diesel engine (maximum power: 3.5 kW at 1500 rpm) connected with an eddy current dynamometer (maximum load: 7.5 kW). The engine exhaust emissions such as hydrocarbon (measuring range: 0-20000 ppm vol), CO (measuring range: 0-10% vol.%), and NO_x (measuring range: 0-500 ppm vol) are recorded using the AVL-444 digas analyzer. The smoke opacity is recorded by the AVL-437 smoke meter. The schematic lay-out of the emission test set-up is shown in fig. 3. The emission assessment has been initially carried out with BD and BD + 30OPO. Since the water concentration in base fuel has a significant contribution emission parameters, three different concentrations of water (5%, 10%, and 15%) are mixed with BD + 30OPO and named BD + 30OPO + 5W, BD + 30OPO + 10W, and BD + 30OPO + 15W, respectively. Based on the previously prepared fuel samples, the evolution of emission characteristics at optimum conditions is studied.

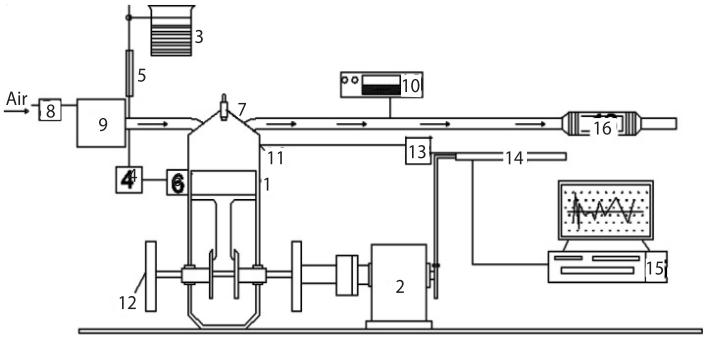

Figure 3. Schematic lay-out of the emission test set-up: *1 – Diesel engine, 2 – eddy current dynamometer, 3 – fuel tank, 4 – filter (fuel), 5 – fuel measurement, 6 – fuel pump, 7 – fuel injector, 8 – air filter, 9 – air stabiliying tank, 10 – emission analyzer, 11 – pressure tranducer, 12 – TDC encoder, 13 – charge amplifier, 14 – indimeter, 15 – monitor, and 16 – silencer*

Results and discussion

Experimental trials and fuel properties

The test fuels are prepared based on the L_9 orthogonal array as mentioned in the Taguchi method and the measured properties are represented in tab. 1. The properties indicate that the inclusion of OPO in pure diesel rises the fuel density and decreases the kinematic viscosity, calorific value, and flashpoint. Generally, the low viscous OPO's calorific value is almost 4% lower than BD, and the emulsion stability will not be affected due to the presence of OPO in base fuel [16]. The water addition in the test fuel reduces the calorific value, flashpoint, and stability period as the hydrocarbon fuel is replaced by an identical amount of water [6]. However, the remaining properties such as fuel density and viscosity are significantly increased with an increase in water level. It is also noted that though the presence of surfactant increases the stability period positively, the other properties exhibit a negative impact concerning high surfactant concentration.

Table 1. Process parameters combinations and corresponding fuel properties

Process Parameters (input)			Responses (output)				
OPO [vol.%]	Water [vol.%]	Surfactant [vol.%]	Density [kgm^{-3}]	Viscosity [mm^{2}s^{-1}]	Calorific value [MJkg^{-1}]	Stability [hours]	Flashpoint [°C]
10	5	0.5	833	3.37	40.32	96	66
10	10	1.0	844	3.38	37.96	90	70
10	15	1.5	854	3.41	35.61	84	75
20	5	1.0	837	3.13	39.97	93	64
20	10	1.5	848	3.15	37.62	87	68
20	15	0.5	853	3.12	35.91	72	72
30	5	1.5	841	2.91	39.63	90	67
30	10	0.5	846	2.87	37.91	75	72
30	15	1.0	857	2.88	35.56	70	76

Grey-relational grade and S/N ratio of fuel properties

By applying the fuel properties value in eqs. (3)-(5), the GRC, GRG, and S/N ratios are evaluated for all the properties, respectively. The values are presented in tab. 2. From the presented value, it is observed that trial Number 1, *i.e.*, 10% OPO, 5% water, and 0.5% surfac-

tant combination in base fuel exhibits a higher value (density, calorific value, and stability period) compared to other combinations. For fuel viscosity, trial number 8 (30% OPO, 10% water, and 0.5% surfactant in BD) exhibits a better value than the other trials. As far as the flashpoint is concerned, trial Number 9, *i.e.*, 30% OPO, 15% water, and 1% surfactant combination provides a safe value. The weightage factor has been assigned for all the properties and the overall GRG and S/N ratio are examined. The report expresses that trial Number 1 provides the overall best fuel quality and is recommended as an initial best setting within the L_9 orthogonal array.

Table 2. Grey-relational grade and S/N ratio of fuel properties

Weight age factor	0.2	0.2	0.2	0.2	0.2	Grey-relational grade	S/N ratio	Position
Trial No.	GRC							
	Density [kgm^3]	viscosity [mm^{2}s^{-1}]	Calorific value [MJkg^{-1}]	Stability [hours]	Flash point [°C]			
1	1	0.3506	1	1	0.3333	0.7367	–2.6530	1
2	0.5217	0.3461	0.5021	0.6842	0.4545	0.5017	–5.9902	6
3	0.3636	0.3333	0.3356	0.52	0.8333	0.4771	–6.4260	7
4	0.75	0.5094	0.8717	0.8125	0.2941	0.6475	–3.7742	3
5	0.4444	0.4909	0.4685	0.5909	0.3846	0.4758	–6.4501	8
6	0.3750	0.5192	0.3505	0.3535	0.5555	0.4303	–7.3239	9
7	0.6	0.8709	0.7752	0.6842	0.3571	0.6575	–3.6419	2
8	0.48	1	0.4968	0.3823	0.5555	0.5829	–4.6872	5
9	0.3333	0.9642	0.3333	0.3333	1	0.5928	–4.541	4

Optimum value of fuel processing parameters and its confirmation test

From the overall GRG value, the optimum level of individual process parameters is identified by using MINITAB software. The main effect plots of the mean and S/N ratio for all three levels are represented fig. 4. The graphical illustrations express that the increase in OPO volume concentration from 10-20%, weakens the overall fuel quality *i.e.*, reduces the GRG and S/N ratio values. However, 30% OPO blended fuel leads to better fuel quality compared to others. As far as the water concentration is concerned, 10% water blended fuel promotes better fuel quality. Surfactant concentration also follows a similar path to water concentration, and a 1% contribution of surfactant shows better fuel quality compared to others. The overall result implies that the BD with 30% OPO, 10% water concentration, and 1% surfactant shows superior fuel quality, and $A_3B_2C_2$ is recommended as an optimum setting.

A confirmation test also has been executed to confirm the fuel quality is improved at the optimum setting by comparing the values with the initial best setting. The comparison of fuel properties at the initial best setting and the optimum setting is represented in tab. 4. At the optimum setting, the fuel density is marginally increased by 1.8% and the viscosity is significantly reduced by 13.7%. The calorific value and stability period of fuel at optimum condition are 4.7% and 15.6% lower than the initial best condition, and an increase of 12.1% in flashpoint is recorded for a flashpoint. Based on the fuel properties at optimum conditions, the grey relational grade and *S*/*N* ratio are experimentally evaluated and compared with the predicted value. The prediction of the *S*/*N* ratio is executed by applying [16]:

$$\hat{y} = y_m + \sum_{i=1}^{o} (\bar{y}_i - y_m) \tag{6}$$

where y_m is the total mean value, and $\bar{y}_I$ is the mean value S/N ratio

At optimum conditions, the confirmation test has been carried out to ensure the overall quality of fuel, and the S/N ratio comparison is represented in tab. 5. The comparison of the initial best setting and optimum setting reflects that the S/N ratio at the optimum setting is increased by 27.5%. Besides, the predicted value has a good agreement with the predicted value.

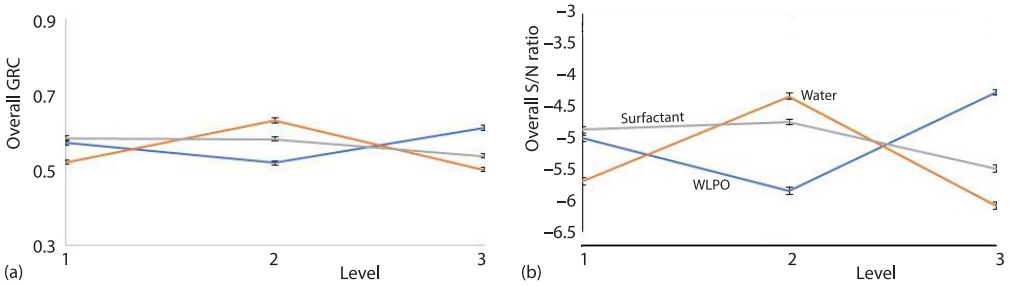

Figure 4. Main effect plots for mean and S/N ratio

Table 4. Comparison of output responses

Test run	Responses (output)				
	Density [kgm^{-3}]	Viscosity [mm^{2}s^{-1}]	Calorific value [MJkg^{-1}]	Stability [hours]	Flashpoint [°C]
Initial best setting – A1B1C1	833	3.37	40.32	96	66
Optimum setting – A3B2C2	848	2.91	38.42	81	74

Table 5. Confirmation test

	Initial best setting	Optimum setting	
Combination	A1B1C1	A3B2C2	
		Predicted value	Experimental value
GRG	0.7367	0.7743	0.7786
S/N ratio	–2.6530	–1.8578	–1.9249
Improvement in S/N ratio [%]		27.5%	

Analysis of variance

The individual contribution of fuel processing parameters on overall fuel quality has been estimated by analysis of variance. From the S/N ratio of individual process parameters and delta value, key parameters such as the total sum of squares (SS_T) and the mean sum of squares (MS_S) have been derived to identify the individual contribution. The SS_T and MS_S are estimated by [16]:

$$SS_T = \sum_{i=1}^{p} (y_i - y_m)^2 \tag{7}$$

$$MS_S = \frac{SS_T}{\text{DoF}} \tag{8}$$

where y_i is a mean response, and y_m is a grand mean value of the collective responses.

The S/N ratio's overall responses and their significance are characterized in tab. 6. The derived values conclude that the water concentration in base fuel plays a major role and has a maximum contribution of 54.41% followed by OPO (30.94% contribution). The surfactant concentration has a lower contribution of 14.65%.

Table 6. The S/N ratio's overall responses and its significance

Level	OPO (A)	Water (B)	Surfactant (C)
1	–5.023	–5.709	–4.888
2	–5.849	–4.356	–4.768
3	–4.29	–6.097	–5.506
Delta	1.559	2.741	0.738
Position	2	1	3
Optimum level	A3	B2	C2
SS_T	0.1578	0.2774	0.0747
MS_S	0.2334	0.4103	0.1104
Contribution [%]	30.94	54.41	14.65

Emission assessment

The emission study has been conducted by using five different fuels to comprehend the improvement of the proposed fuel. The emission parameters of test fuels evaluated under peak BMEP conditions are represented in fig. 5. The results imply that the HC and CO emissions are significantly reduced while the OPO is blended with BD. The higher amount of oxygen offered by the low viscous citrus fuels promotes the combustion reaction and reduces the formation of HC and CO emissions [14, 26]. The BD blended with 30% OPO reduces the HC formation by 15.4% compared to BD, whereas the CO emission is dropped by 25%. The water concentration has been added from 5-15% in the base fuel combination (BD + 30OPO) with an interval of 5%. The HC and CO emission assessments indicate that these emissions are gradually reduced up to 10 % water inclusion and this trend is reversed for 15% water. The strength of micro-explosion and secondary atomization of water emulsion fuel is adequate to

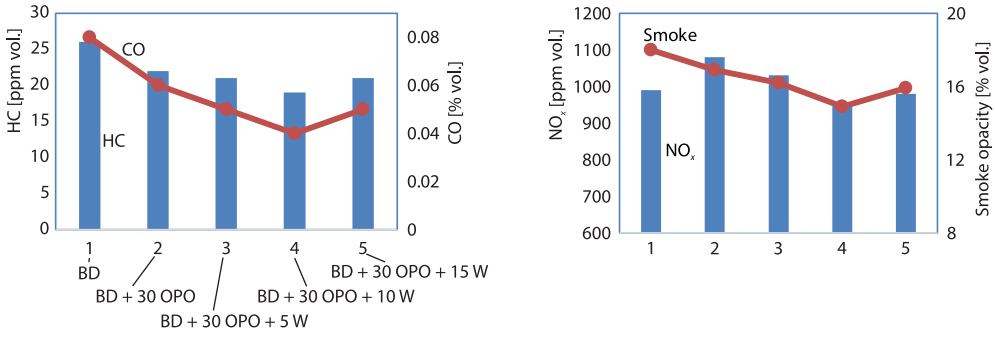

Figure 5. Emission progress of test fuels

diminish the ignition delay period effects and leads to complete combustion with improved energy and emission performances. However, the more latent heat evaporation of water particles due to higher water concentration leads to poor combustion performances [13, 20]. The base fuel combination with 10% water reduces the HC and CO emissions by 26.9% and 49% compared to BD, respectively. The smoke opacity of the fuel also follows a similar track of HC and CO emissions while the oxygenated fuel and water are blended with base fuel [26]. The smoke opacity of OPO blended BD is 6.2% lower than BD and this emission is further reduced to 17.3% while adding 10% water.

The NO_x emission of oxygenated fuel *i.e.*, OPO blended BD emits more amount of NO_x emission due to the high local combustion temperature [6, 22]. The base fuel combination's NO_x emission is 9.1% higher than conventional BD. The presence of water in base fuel reduces the local combustion flame temperature and reduces the NO_x formation since the water particles absorb more amount of heat during evaporation. The NO_x emission is also gradually reduced with an expansion of water (up to 10%), and a drop of 12.1% in NO_x emission is reported by BD + 30OPO + 10W emulsion fuel compared to the base fuel combination. Above 10% water concentration, the NOx emission trend also is in a negative direction as the longer ignition delay period of highly intense water significantly affects the normal combustion process [20].

Conclusions

Energy from the waste orange peels has been extracted and the chemical constituents have been perceived. A multi-response optimizationol (grey-relational based) has been implemented to permute the OPO as a sustainable and greener energy source for biofuel application by blending the optimum quantity of water and surfactant. The emission progress of test fuels is also evaluated under peak BMEP conditions. Based on this study, the conclusions are as follows.

- A stable emulsion fuel can be formulated using OPO, water, and sorbitan monolaurate surfactant in base fuel effectively.
- The base diesel blended with 30% OPO, 10% water, and 1% surfactant promotes superior fuel quality and is recorded as the optimum setting. The fuel quality is improved by 27.5% at the optimum setting.
- The water concentration has a major contribution overall fuel quality (54.41%) followed by OPO concentration (30.94%), and surfactant concentration (14.65%).
- At optimal conditions, the exhaust emissions such as HC, CO, and smoke are reduced by 26.9%, 49%, and 17.3%, respectively.
- The NO_x formation has been increased by 9.1% while adding the OPO in BD. However, a drop of 12.1% NO_x emission is acknowledged for the fuel prepared at optimum condition compared to BD + 30OPO.

Overall, it can be concluded that the OPO along with the optimized quantity of water and surfactant in base fuel will be considered a sustainable and greener energy source for biofuel applications.

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