

Correlative HHV prediction from proximate and ultimate analysis of char obtained from co-cracking of residual fuel oil with plastics

Pamreishang Kasar and Md. Ahmaruzzaman[†]

Department of Chemistry, National Institute of Technology, Silchar 788 010, India

(Received 8 November 2020 • Revised 25 February 2021 • Accepted 21 March 2021)

Abstract—It is imperative to know the energy content of the char to ascertain its application, which is environmentally friendly and efficient. In this context, the higher heating values (HHV) of the char resulting from the co-cracking of residual fuel oil (RFO) with various other waste plastics have been determined experimentally. Experimental results of the proximate and ultimate analysis of the char obtained from the co-cracking process were used to estimate the higher heating values (HHV) using eight different correlation models. The char obtained from the co-cracking of RFO and polypropylene (PPI) was found to have higher heating values (HHV) of 31.02 MJ/kg, while the HHV of Bakelite (BL) showed 23.56 MJ/kg. The best among the proximate correlations considered in this study resulted in the coefficient (R^2) of 0.971, the average bias of -0.68% , and absolute error of 1.70% . The most relevant among the ultimate correlation models resulted in the coefficient of determination (R^2) of 0.980, whereas the average and absolute bias errors were found to be -1.29% and 0.25% , respectively. The proximate and ultimate analysis of the chars reveals a direct interaction between the reactive species during the co-cracking of RFO with various types of plastic waste used in the study.

Keywords: Co-cracking, Char, Residual Fuel Oil (RFO), Higher Heating Value (HHV), Proximate Analysis

INTRODUCTION

The recycling of plastics waste through the thermal cracking process is regarded as essential due to the environmental pollution that is prevailing. The thermal process of recycling has opened up a new area of scope and challenges in the field of renewable energy too. The co-cracking of plastics with other materials, such as biomass, coal, heavy oil, has gained increasing recognition as a means of alternative energy recovery route. Co-cracking of plastics with other materials, such as vacuum residues with waste plastics [1], biofuels and plastics [2], waste oil lubricant with mixed plastics [3], and gas oil with plastics [4] has been investigated by many researchers. However, to the best of our knowledge, there are no literatures pertaining to the co-cracking of residual fuel oil with waste plastics [5]. Further, no literature data are available on the proximate and ultimate analysis correlated with predictive model of the HHV of the char obtained from the co-cracking of residual fuel oil with plastics.

The co-cracking of RFO and waste plastics has been found to be a promising alternative source of fuel energy [6]. This is also a prospective means of waste management beside exploring through analysis to account for the possible application of the attractive product pattern resulting from the co-cracking process [7]. Similar to our earlier studies [6,7] we have carried out the co-cracking of RFO and waste plastics and char product is one of the end product of the process. The results obtained here may have implications on understanding the chemical reactions and chemical alteration during the co-cracking process between the various waste plastics and residual oil.

Characterization of the liquid, coke, and gaseous products obtained from the co-cracking experiment was necessary to choose the end use of the products. For instance, the coke obtained from the co-cracking process may have many applications. These types of coke obtained from the co-cracking (with or without activation) were used to eliminate toxic substances of polluted wastewater for its purification—the carbon residue like activated carbon, slurry, bottom ash, carbon, etc. [5-7]. The char product resulting from the coprocessing of plastics and residual fuel oil may have the prospective to be used in the gasification to generate producer gas, fired to elevate steam for generation of power, to make carbon material, needle coke, graphite.

The ultimate and proximate analysis of coke/char resulting from the co-cracking process can give greater insight into their properties and yield useful information for their clean and efficient utilization. Alternatively, the calorific value or higher heating value (HHV) of coke product establishes the quantitative heat energy content of these fuels which, as determined by the standard method using bomb calorimeter, is not an easily accessible approach. There is an alternative way of determining the HHV of the coke through correlation that can predict the HHV from the ultimate analysis of the fuel [11] and even from both the proximate and ultimate analyses [9,10]. This correlation has been recognized to be exceptionally useful in the modelling of thermal systems. However, it has a significant disadvantage since it is necessary to have the elemental analysis input data, which requires an expensive apparatus and is highly dependent on the operator skills to render acceptable results [11-13]. There are also few correlations available in the literature based on the proximate analysis of the solid fuels [11,12,14-16]. Unfortunately, it is not universally applicable and limited to a single type of solid fuel of a specific region only. However, various correlations

[†]To whom correspondence should be addressed.

E-mail: mda2002@gmail.com

Copyright by The Korean Institute of Chemical Engineers.

were tested for their applicability for a broader range of fuels by Krevlen and Schuyer [20]. This article determined the caloric values of the char obtained from the co-cracking of RFO with waste plastics experimentally and correlated with some of the selected models based on the proximate and ultimate analyses to predict the HHV of the coke (solid fuel) from the co-cracking of waste plastics with residual fuel oil. The details of the process and experimental setup were reported in our previous study [7] and established the proximity of the heating values obtained from the experiment to that of the theoretical values predicted using proximate and ultimate analyses correlation models.

MATERIALS AND METHODS

The batch reactor used in the study was first flushed with nitrogen after the sample was loaded in the reactor chamber using a crucible type container and heated to the required temperature of 500 °C. The feedstocks include residual fuel oil (RFO), polypropylene (PPI) injection grade, polypropylene (PPX) extrusion grade, high-density polyethylene (HDPE), and Bakelite (BL). These samples were pyrolyzed in individual, their binary (1/1, wt %), ternary (1/1/1, wt%), quaternary (1/1/1/1, wt%), and quinary (1/1/1/1/1, wt%), whereby the feeds were subjected to heat for two and half hours (2.5 h) inside the reactor. The coke/char that remained were gathered from the beneath of the reactor after the experiment was completed. The details of the construction of the batch reactor and experimental process have been reported elsewhere [18,19].

The coke/char products from the co-cracking process were characterized by proximate analysis methods using a muffle furnace (optical technology), hot air oven (optical technology), and digital balance as per ASTM D 3172-73(84) (1989) [20] standard. The volatile contents in the sample was calculated in accordance with the ASTM D 3175-89 (1989) [21] methods of sparking the fuels. The moisture present in the coke samples was measured using procedures in the Sartorius infrared moisture meter in concurrence with the method according to the ASTM D 3173-87 (1989) [22], and lastly, the ash content of the coke samples was analyzed as per the ASTM D 3174-89 (1989) [23] methods in the electrical muffle furnace, while the fixed carbon was computed by difference, using the

formula in Eq. (i). The proximate analysis and measurement of HHV were performed not less than three times to ensure reproducibility of the experimental data.

$$\text{Fixed carbon \%} = 100 - (\text{moisture \%} + \text{ash \%} + \text{volatile matter \%}) \quad (i)$$

The ultimate analysis of the sample was as per the ASTM Standard D 3176 to (3179-3184) and carried out using Elemental Analyzer, make/model: Eurovector EA3000. While the experimental calorific value of the char was determined using Bomb calorimeter with 1108P oxygen bomb and 6775 digital thermometers, make Parr Instrument Co. USA, model: Catalogue No. 13341EE, with working principle Isoperibol, Dynamic and time-controlled system having repeatability (% RSD) of 0.20, with a temperature resolution of 0.002 °C and accuracy of 0.3% and can measure up to 12000 Calories value measurement. Test procedure to determine the HHV values of the char was carried out as per the ASTM D5865-13 standard methods.

The proximate and ultimate analysis data obtained from the experiment were fitted into the eight mathematical Models as shown in Tables 1 and 2 by regression analysis to predict the HHV of the char. The method of minimizing the error squared and least square was applied to assess the adjustable parameters of each equation. The correlation is considered to be the best-fitted regression line if the error of the estimation tends to zero [25]. In our study, we considered the coefficient of determination (R^2) to select the most suitable correlation equation from among the four number of models chosen each for proximate and ultimate analysis (Tables 1 and 2). A total of eight correlation models were used to calculate heating values of the char obtained from the co-cracking process and compared with that of the experimentally determined values obtained from the Bomb calorimeter. There are numerous correlation models available in the literature; however, there are variations in the nature and characteristics of the chars for which the correlation models were designed. Therefore, it is important to understand the similarity in the characteristics of the material for which particular model has been derived. Thus, we can choose the most related material and hence the correlative model designed for these materials to fit in our analysis data for similar applications. However, it is necessary to know the experimental calorific value at the first

Table 1. Equations used in the prediction of HHV of char from proximate analysis

Sl no.	Equation	Reference
1	$\text{HHV} = 0.3536\text{FC} + 0.1559\text{VM} - 0.0078\text{ASH}$ (MJ/kg)	(1) [27]
2	$\text{HHV} = 0.3543\text{FC} + 0.1708\text{VM}$ (MJ/kg)	(2) [14]
3	$\text{HHV} = 0.196\text{FC} + 14.119$ (MJ/kg)	(3) [18]
4	$\text{HHV} = 35.43 - 0.1835\text{VM} - 0.3543\text{ASH}$ (MJ/kg)	(4) [14]

Table 2. Equations used in the prediction of HHV of char from ultimate analysis

Sl no.	Equation	Reference
1	$\text{HHV} = 0.3383\text{C} + 1.443(\text{H} - \text{O}/8) + 0.0942\text{S}$ (MJ/kg)	(5) [28]
2	$\text{HHV} = 0.328\text{C} + 1.419\text{H} + 0.0928\text{S}$ (MJ/kg)	(6) [11]
3	$\text{HHV} = 151.2\text{C} + 499.77\text{H} + 45\text{S} - 47.7\text{O} + 27\text{N}$ (Btu/lb)	(7) [28]
4	$\text{HHV} = 145.44\text{C} + 620.28\text{H} + 40.5\text{S} - 77.54\text{O}$ (Btu/lb)	(8) [29]

Table 3. Proximate analysis of the solid product (char) obtained from the co-cracking of RFO with various types of plastics (dry basis) at 500 °C

Sl no.	Sample particulars	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	VM/FC	Ash content (%)
1	RFO	0.12	21.95	67.12	0.33	10.81
2	PPX	0.20	6.45	77.46	0.08	15.90
3	BL	0.05	20.21	54.56	0.37	25.18
4	PPI	0.25	7.23	77.57	0.09	14.95
5	HDPE	0.20	16.54	72.10	0.23	11.16
6	RFO+PPI	0.47	14.20	82.00	0.17	3.33
7	RFO+PPX	0.78	13.65	81.25	0.17	4.32
8	RFO+BL	1.24	21.05	56.69	0.37	21.03
9	RFO+HDPE	0.79	12.50	80.18	0.16	6.53
10	RFO+PPI+PPX	0.11	12.68	79.67	0.16	7.54
11	RFO+PPI+BL	1.50	16.30	65.57	0.25	16.63
12	RFO+PPI+HDPE	0.54	16.15	70.21	0.23	13.10
13	RFO+PPI+HDPE+BL	0.35	19.25	64.72	0.30	15.68
14	RFO+PPI+PPX+HDPE+BL	0.12	14.68	73.12	0.20	12.08

instance in order to compare and verify the applicability of the model in our study. The models listed in Tables 1 and 2 were selected based on these criteria.

The model yielding the highest value of R^2 was considered the most appropriate one for predicting the HHV of the type of fuel sample from their proximate and ultimate analyses. This is because R^2 values determine the degree of acceptability of the projected correlation [8,25]. The result and hence the derivative conclusion were validated by an error analysis of average absolute error (AAE) and average bias error (ABE) as shown in Eqs. (ii) and (iii), respectively. This also helps to choose the most appropriate correlation equation and are defined as follows:

$$\text{Average absolute error} = \frac{1}{n} \sum_{i=1}^n \left| \frac{\text{HHV}_c - \text{HHV}}{\text{HHV}} \right| \times 100\% \quad (\text{ii})$$

$$\text{Average bias error} = \frac{1}{n} \sum_{i=1}^n \left| \frac{\text{HHV}_c - \text{HHV}}{\text{HHV}} \right| \times 100\% \quad (\text{iii})$$

HHV and HHV_c represent each fuel sample's heating values from the experiment and calculation, respectively, and n is the number of sample data points used for the regression analysis.

Further, the calorific values are defined by the energy released on burning one unit mass of fuel in the presence of surplus air. Calorific value for the char/coke resulting from the co-cracking of RFO with waste plastics was determined experimentally using a Bomb calorimeter. Bomb calorimeter with 1108P oxygen bomb and 6775 digital thermometers, made by Parr Instrument Co. USA, model: Catalogue No. 13341EE, with working principle Isoperibol, time-controlled and dynamic system was used to determine the calorific values of the fuel samples.

RESULT AND DISCUSSION

1. Proximate Analysis

The proximate analysis of the solid fuel product (char) obtained

from the co-cracking of various plastics and heavy oil residue RFO is shown in Table 3. The characteristics of the char in terms of its composition in the form of moisture (M), ash (A), fixed carbon (FC), and volatile matter (VM) content show that the most dominant fraction of the sample was made of volatile matter and fixed carbon with an average of 15.85% and 71.40 %, respectively. The heating values of the coke are directly proportional to their carbon and hydrogen content. Therefore, even though the quantity of ash present in the samples played a significant role in evaluating the higher heating value (HHV) of the samples, the result appears to show that HHV is the function of volatile matter (wt%) and fixed carbon (wt%). A similar observation was made by Ahmaruzzaman [1].

To know the content of moisture, volatile matter, fixed carbon, and ash of the chars resulting from the co-cracking of plastics with RFO is of utmost importance in choosing the clean and most efficient application and hence utilization of the char. Usually, when the char is dominated by volatile matter, the coke/char could have greater reactivity for combustion and gasification. The ash content in the coke indicates the predominance of minerals in the char even though it could have its own problems. The content of the char reported in Table 3 analyzed by the proximate analysis shows that the volatile matter, ash content, and VM/FC ratio of RFO decreases with an increase in temperature. In contrast, the fixed carbon increases with an increase in temperature. This result indicates that while there could have been an evolution of the volatile matter at a lower temperature, it may decrease with increase in temperature anywhere above the pyrolytic temperature of 500 °C. This may be explained by the fact that primary reaction of cracking/pyrolysis was completed at the first stage and can be seen in the volatile matter content of RFO (500 °C) with 21.95% as shown in Table 3. The pyrolysis conditions, including temperature, influenced the reactivity of the char. The char obtained at a lower temperature has a higher reactivity than that obtained at a higher temperature. Further, from Table 3, higher volatile matter (VM) content in the char was shown by RFO, BL, and HDPE with 21.95%, 20.21%, and 16.54%, respec-

Table 4. Ultimate analysis of the solid product (char) obtained from the co-cracking of RFO with various types of plastics (dry basis) at 500 °C

Ultimate analysis		Element particulars %				
Sl no.	Sample particulars	C	H	N	S	O
1	RFO	66.29	3.67	1.73	4.21	1.53
2	PPX	67.57	4.25	0.07	0.10	2.31
3	BL	50.51	5.10	0.00	0.39	2.39
4	PPI	65.74	4.62	0.06	0.48	1.41
5	HDPE	67.57	4.13	0.51	1.07	0.79
6	PPI+RFO	71.25	4.39	0.85	1.93	1.01
7	PPX+RFO	73.25	4.15	0.73	0.85	1.51
8	RFO+BL	55.13	3.96	0.81	1.07	5.25
9	RFO+HDPE	71.21	3.90	1.05	1.23	1.08
10	RFO+PPI+PPX	69.11	3.75	0.53	0.95	1.90
11	RFO+PPI+BL	63.51	3.10	0.77	1.58	4.35
12	RFO+PPI+HDPE	66.07	4.05	0.85	1.56	1.59
13	RFO+PPI+HDPE+BL	64.13	3.95	0.87	1.31	3.47
14	RFO+PPI+PPX+BL+HDPE	68.91	3.56	0.63	1.33	3.57

tively. However, the content of volatile matter in the char directly impacts the reactivity of the char, so the char with higher volatile matter is more reactive than with the lower content of volatile matter. Subsequently, the chars from RFO, BL, and HDPE will have higher reactivity and could be used for combustion and gasification. It was reported that active site gasification is created on the coke when the volatiles are released [30]. Therefore, the lower the volatile matter content of the char, the lower its reactivity. Further, the decrease in the volatile concentration of the pyrolyzed char may be due to the presence of a small concentration of aliphatic compounds [1] and higher selective adsorption of large aromatic hydrocarbons on the other chars. This is because the energy of adsorption on the carbonaceous surface by aromatic compounds is higher than that of aliphatic or olefinic compounds [31].

2. Ultimate Analysis

The ultimate analysis of char resulting from the co-pyrolysis of RFO with different types of plastics is reported in Table 4. The elemental composition of the char is dominated by carbon (C) followed by hydrogen (H) and oxygen (O), while the least elemental constituent of the char was nitrogen (N) followed by sulfur (S). The ultimate analysis results are summarized in Table 5 and show that carbon content ranges from 50.51 (PPI) to 73.25% (PPX+RFO), for hydrogen content ranges from 3.1 (RFO+PPI+PF) to 5.1% (PPI), the nitrogen content of the char samples from 0% (BL) to 1.73%

Table 5. Range of elemental composition and heats of combustion

Parameters	Min. value	Mean value	Max. value
Carbon (C) (%)	50.51	65.73	73.25
Hydrogen (H) (%)	3.1	4.04	5.1
Nitrogen (N) (%)	0	0.68	1.73
Sulphur (S) (%)	0.1	1.29	4.21
Oxygen (O) (%)	0.79	2.30	5.25
HHV (MJ/kg)	23.56	28.12	30.68

(RFO). However, the sulfur content was in the range of 0.1 (BL) to 4.21% (RFO), while the oxygen content was in the range of 0.79 (HDPE) to 5.25% (RFO+PF). Thus, the HHV of the char obtained from the co-cracking process is a function of carbon and hydrogen or both [32].

Table 4 shows that the carbon content of BL was the least among all the samples studied. However, the oxygen content, which also accounts for the lower calorific value, clearly indicates that the BL has the lowest calorific values among the feedstocks used (Table 6).

3. Analysis of Regression and Relative Error for the Predicted HHV

Both experimental and predicted HHV obtained by fitting the data point of proximate analysis into the proximate correlation equa-

Table 6. Experimental and theoretical HHV of chars obtained from the co-cracking of RFO with various types of plastics waste (MJ/kg)

Sample particulars	Experimental (MJ/kg)	Theoretical (MJ/kg)
RFO	28.12	-
PPX	28.90	-
BL	23.56	-
PPI	29.20	-
HDPE	28.64	-
RFO+PPI	31.02	28.66
RFO+PPX	30.68	28.51
RFO+BL	24.65	25.84
RFO+HDPE	30.12	28.38
RFO+PPI+PPX	29.46	28.74
RFO+PPI+BL	25.87	26.96
RFO+PPI+HDPE	28.12	28.65
RFO+PPI+HDPE+BL	27.14	27.38
RFO+PPI+PPX+HDPE+BL	28.20	27.69

Table 7. Predicted HHV using the proximate analysis data of chars obtained from the co-cracking of RFO with various types of plastics waste and its experimental values (MJ/kg)

Sl no.	Sample particulars	Experimental value	From Eq. (1)	From Eq. (2)	From Eq. (3)	From Eq. (4)
1	RFO	28.12	27.07	27.53	27.27	27.57
2	PPX	28.90	28.27	28.55	29.30	28.61
3	BL	23.56	22.25	22.78	24.81	22.80
4	PPI	29.20	28.44	28.72	29.32	28.81
5	HDPE	28.64	27.99	28.37	28.25	28.44
6	RFO+PPI	31.02	31.18	31.48	30.19	31.64
7	RFO+PPX	30.68	30.82	31.12	30.04	31.39
8	RFO+BL	24.65	23.16	23.68	25.23	24.12
9	RFO+HDPE	30.12	30.25	30.54	29.83	30.82
10	RFO+PPI+PPX	29.46	30.09	30.39	29.73	30.43
11	RFO+PPI+BL	25.87	25.60	26.02	26.97	26.55
12	RFO+PPI+HDPE	28.12	27.24	27.63	27.88	27.83
13	RFO+PPI+HDPE+BL	27.14	25.76	26.22	26.80	26.34
14	RFO+PPI+PPX+BL+HDPE	28.20	28.05	28.41	28.45	28.46

Table 8. Predicted HHV using the ultimate analysis data of chars obtained from the co-cracking of RFO with different types of plastics waste and its experimental values (MJ/kg)

Sl no.	Sample no.	Expt. value	From Eq. (5)	From Eq. (6)	From Eq. (7)	From Eq. (8)
1	RFO	28.12	27.84	27.34	27.96	27.84
2	PPX	28.90	28.08	28.20	28.15	28.08
3	BL	23.56	24.05	23.84	23.47	24.05
4	PPI	29.20	28.70	28.16	28.39	28.70
5	HDPE	28.64	28.78	28.12	28.62	28.78
6	PPI+RFO	31.02	30.43	29.77	30.30	30.43
7	PPX+RFO	30.68	30.57	29.99	30.55	30.57
8	RFO+BL	24.65	24.39	23.75	24.08	24.39
9	RFO+HDPE	30.12	29.64	29.01	29.65	29.64
10	RFO+PPI+PPX	29.46	28.54	28.08	28.59	28.54
11	RFO+PPI+BL	25.87	25.32	25.38	25.67	25.32
12	RFO+PPI+HDPE	28.12	28.06	27.56	27.98	28.05
13	RFO+PPI+HDPE+BL	27.14	26.89	26.76	26.95	26.89
14	RFO+PPI+PPX+BL+HDPE	28.20	27.93	27.77	28.15	27.93

Table 9. Proximate Correlation models and regression analysis along with the relative error %

Equations (MJ/kg)	R ²	Relative error (%)	
		Average absolute error (AAE)	Average bias error (ABE)
HHV=0.3536F+0.1559VM-0.0078 Ash (1)	0.971	2.55	-2.04
HHV=0.3543FC+0.1708VM (2)	0.971	1.70	-0.68
HHV=0.196FC+14.119 (3)	0.936	1.92	0.24
HHV=35.43-0.1835VM-0.3543ASH (4)	0.962	1.80	0.06

tion is shown in Table 7. The experimental and predicted HHV obtained by fitting the ultimate analysis data point of into the ultimate correlation equation are given in Table 8. The resulting average absolute errors given were 2.55, 1.70, 1.92, and 1.80%, respectively

(Table 9).

The average bias errors were found to be -2.04, -0.68, 0.24, and 0.06%, respectively. The least discrepancies between the experimental and predicted values of HHV obtained from the proximate

analysis of the char were observed in Eq. (2) and, therefore, would be considered the best correlation among all the models explored in the study. It was found that the HHV of the char obtained from the co-cracking of RFO+PPI, RFO+PPI+PPX, RFO+PPI+HDPE+BL, and RFO+PPI+PPX+BL+HDPE was 31.02, 29.46, 27.14, and 28.20 MJ/Kg, respectively. Therefore, it is concluded that the chars resulting from the co-cracking of RFO with various types of plastics possess a good heating value. Therefore, the char obtained from the co-cracking process has the potential to be used as an alternate energy source, thereby culminating with the waste plastics as useful energy resources without any wastage through the cracking/pyro-

lysis process of recycling.

The list of the models used in predicting the HHV of the char in correlation with the proximate analysis data and the coefficient of determination (R^2) is provided in Table 9. The R^2 values were within the range of 0.936 to 0.971, which is logically very high for the models and could be applicable with a satisfactory result. However, to avoid complications in further mathematical analysis, a practical model should always be simple. Among the models (Table 9) used in the study, Eq. (2) ($\text{HHV} = 0.3543\text{FC} + 0.1708\text{VM}$ MJ/kg) was the best model with the highest R^2 value of 0.971, with absolute and bias error of 1.70 and -0.68% , respectively. In accordance

Table 10. Ultimate Correlation models and regression analysis and the relative error %

Equations	R^2	Relative error (%)	
		Average absolute error (AAE)	Average bias error (ABE)
$\text{HHV} = 0.3383 \text{ C} + 1.443 (\text{H} - \text{O}/8) + 0.0942\text{S}$ MJ/kg	(5) 0.975	0.09	-1.09
$\text{HHV} = 0.328 \text{ C} + 1.419 \text{ H} + 0.0928 \text{ S}$ MJ/kg	(6) 0.973	0.37	-2.46
$\text{HHV} = 151.2 \text{ C} + 499.77\text{H} + 45\text{S} - 47.7\text{O} + 27 \text{ N}$ Btu/lb	(7) 0.980	0.25	-1.29
$\text{HHV} = 145.44 \text{ C} + 620.28 \text{ H} + 40.5\text{S} - 77.54 \text{ O}$ Btu/lb	(8) 0.975	0.09	-1.09

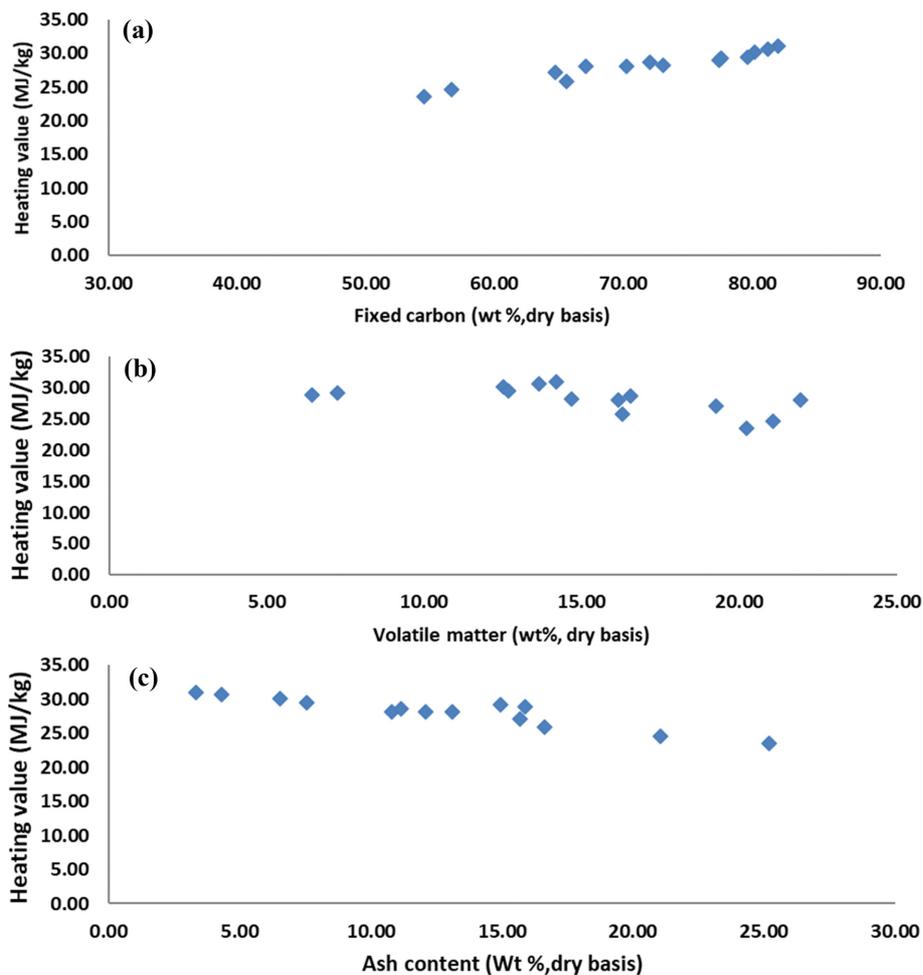


Fig. 1. (a) Correlation between the fixed carbon content and HHV of char, (b) correlation between the volatile matter and HHV of char, (c) Correlation between the ash content and HHV of char.

with the models in our study, the fixed carbon and volatile matter content of the char has a positive impact on the HHV, while the ash content has a more or less negative impact.

However, the validation of the Eqs. (5)-(8) in the prediction of the HHV of the char by fitting in the ultimate analysis data resulted in an average absolute error (AAE) percent in the range of 0.09 to 0.37%. While the average bias error was in the range of -2.46 to -1.09% with the R^2 value from 0.973 to 0.980 as reported in Table 10. These results clearly suggested that Eq. (7) ($151.2 C + 499.77H + 45S - 47.7O + 27 N \text{ Btu/lb}$) with an R^2 value of 0.980, AAE value of 0.25%, and ABE value of -1.29% was the best model among all the models chosen to validate the HHV prediction from the ultimate analysis data. Table 4 indicates that the primary factors impacting the HHV of the char using the selected equations are carbon, hydrogen, and oxygen.

4. The Calorific Value of Char Obtained from the Co-cracking of RFO with Waste Plastics

The calorific values of chars obtained from the cracking individual RFO and waste plastic (PPX, PPI, HDPE, and BL) along with the chars resulting from the co-cracking of these materials were determined by bomb calorimeter. The co-cracking process was also carried out in binary, ternary, quaternary, and quinary combination maintaining a blending ratio of 1 : 1 in all the cases of mixtures. Both the experimental and theoretical calorific values were compared and given in Table 6. In most of the cases, the experimental values were higher than that of the theoretical HHV, suggesting

that the co-cracking of RFO with the waste plastics gave rise to a reaction resulting in a synergistic effect, which may also have been influenced by the temperature and catalyst used in the process.

The char obtained from the cracking of individual RFO and all other waste plastics has shown good calorific values except BL (which has fairly lower calorific value than the rest) as evident from Table 6. The calorific values of the char obtained from the mixture containing BL were found to be low among all the samples studied.

5. Comparison between Experimental and Predicted HHV Using Proximate Correlation Equation and Factors Affecting the HHV

Fig. 2 shows the comparison between the theoretical and experimental values of the volatile matter content of the char obtained from the co-cracking of RFO with different types of plastics. The empirical volatile matter content of the char resulting from the co-cracking of RFO+PPX, RFO+BL, and RFO+HDPE was found to be lower than that of the theoretical average values.

However, in the case of RFO+PPI, the experimental value of VM content of the char was higher than that of the theoretical average value.

A similar observation was also made for the VM content of char obtained from co-cracking of RFO+PPI+PPX, RFO+PPI+BL, RFO+PPI+HDPE, RFO+PPI+HDPE+BL, and RFO+PPI+PPX+BL+HDPE. A comparative study of theoretical and experimental values of the fixed carbon content of the char is shown in Fig. 3. It is found that all the chars obtained from the co-cracking of RFO

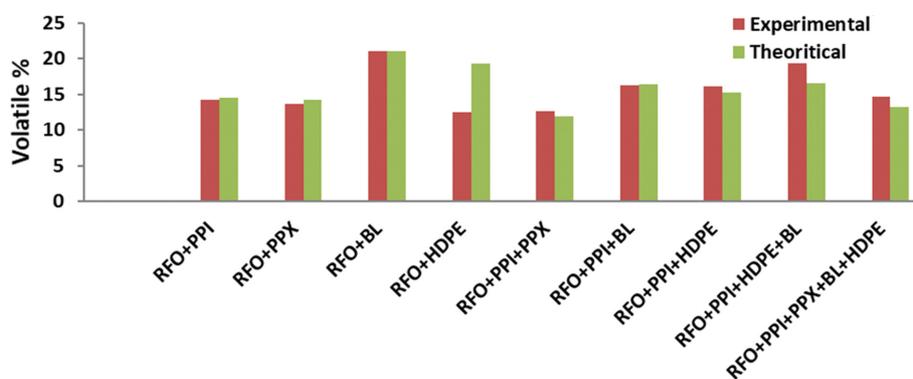


Fig. 2. Comparison of experimental and theoretical volatile matter of chars obtained from the co-cracking of RFO with various waste plastics.

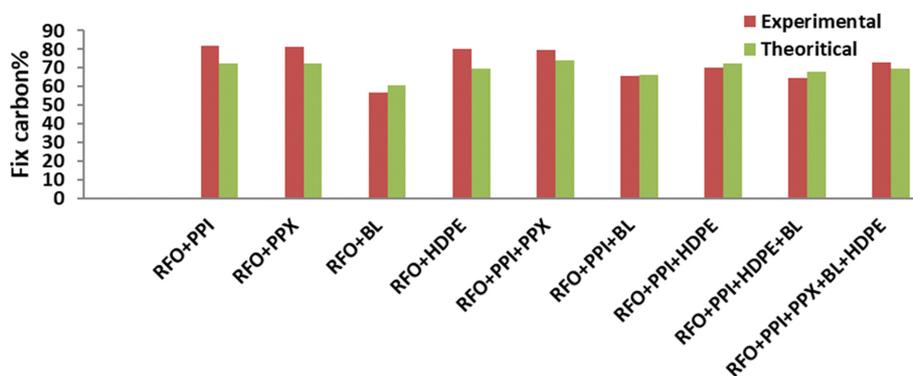


Fig. 3. Comparison of experimental and theoretical fixed carbon content of chars obtained from the co-cracking of RFO with various waste plastics.

with various plastics except with Bakelite (RFO+BL) showed higher experimental values than that of their theoretical average values, indicating an interaction between the feedstock (RFO) and different plastics co-cracked together. Further, the char obtained from the cracking of RFO was found to have an ash content of 10.8% as shown in Table 3.

The manufacturing of carbon electrodes for aluminum refining requires a highly pure carbon with low ash content and free from sulfur [1]. Therefore, the char obtained from the cracking/pyrolysis of RFO could be a prospective material in the manufacture of carbon electrodes after removal of sulfur from the char.

Therefore, it is recommended to further study the sulfur content of the char obtained from the co-cracking process. There was no char product obtained from the cracking of PPI. A similar result was reported [33], while a low percentage (3%) of char was formed in the case of PPX. This variation from PPI may be due to the additive used during its primary processing and impurities as waste material, as it is source dependent. However, the char obtained from the co-cracking of RFO+PPX and RFO+PPI has been observed to contain low ash of 3.33% and 4.32%, respectively. The comparative results of the theoretical and experimental value of ash content in the char or coke obtained from the co-cracking of RFO with various types of plastics are given in Fig. 4. The char obtained from the binary co-cracking of RFO with PPI, PPX, and HDPE was found to demonstrate a higher theoretical value (average of the two individuals) of ash content than their experimental values. A similar observation was made in the case of RFO+PPI+PPX and RFO+

PPI+PPX+BL+HDPE. However, in the case of co-cracking of RFO+BL (the lowest increase of 16.86%), RFO+PPI+BL, RFO+PPI+HDPE (with a maximum increase of 78.91%), and RFO+PPI+HDPE+BL, the experimental values were higher compared to the theoretical average values of the feedstocks. This outcome has clearly shown that the char resulting from the cracking of RFO are able to entrap some portion of the ash/metals present in the other feedstocks of waste plastics, which otherwise would have escaped in the liquid products. From Fig. 1, fundamental interrelations were examined between the heating values of the char and experimental data (FC, VM and Ash) obtained from the proximate analysis.

The higher heating values indicate a low correlation with the volatile matter (Fig. 1(b)). It is evident that the samples with lower content of ash and higher content of fixed carbon could have a relatively higher heating value (Fig. 1(a) & Fig. 1(c)). The key factors which influenced the heating values of the char would be the volatile and fixed carbon content of the char. The char product from the co-cracking of RFO+PPI and RFO+PPX have been found to contain lower volatile matter of 14.20% and 13.65%, respectively, and may be accredited to the presence of a small concentration of aliphatic compounds. Moreover, their theoretical average values are smaller than that of the experimental values.

6. Comparison between Experimental and Predicted HHV Using Ultimate Correlation Equation and Factors Affecting the HHV.

Comparison between theoretical and experimental elemental content of the char resulting from the co-cracking of RFO with plas-

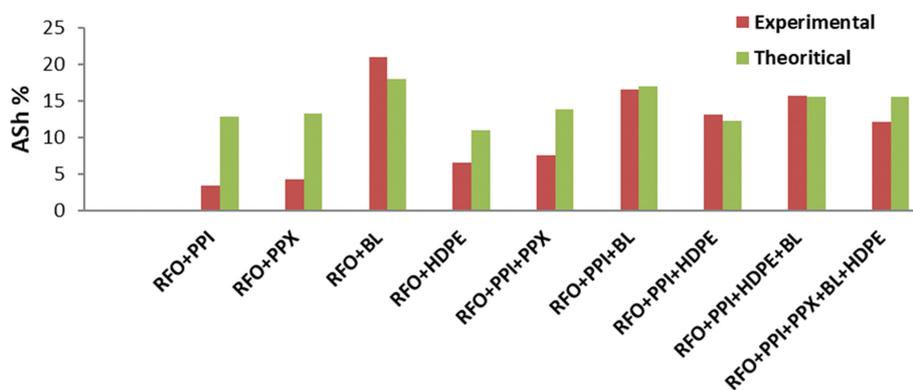


Fig. 4. Comparison of experimental and theoretical ash content of chars obtained from the co-cracking of RFO with various waste plastics.

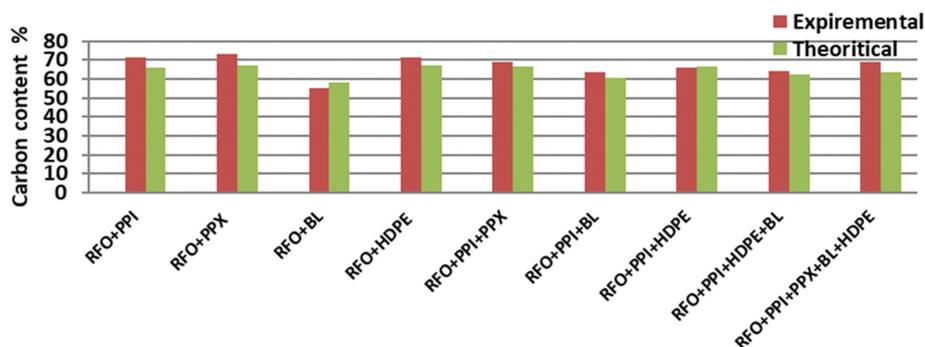


Fig. 5. Comparison of experimental and theoretical carbon content of chars obtained from the co-cracking of RFO with various waste plastics.

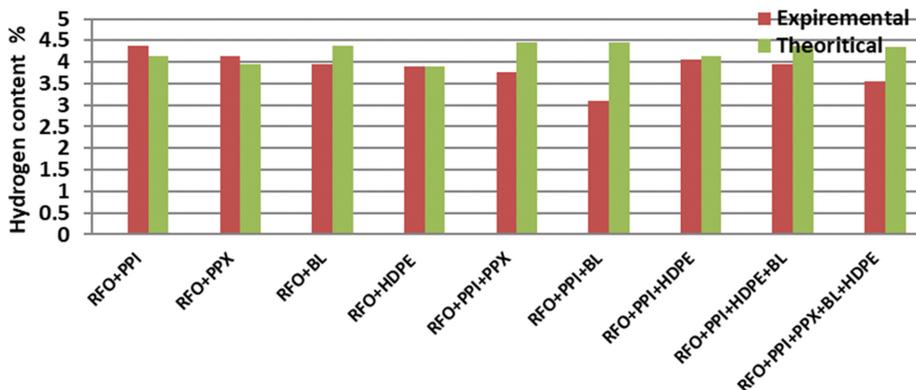


Fig. 6. Comparison of experimental and theoretical hydrogen content of chars obtained from the co-cracking of RFO with various waste plastics.

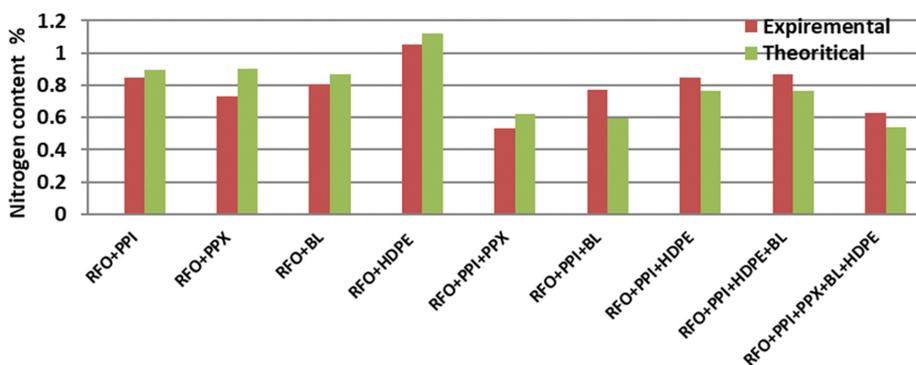


Fig. 7. Comparison of experimental and theoretical nitrogen content of chars obtained from the co-cracking of RFO with various waste plastics.

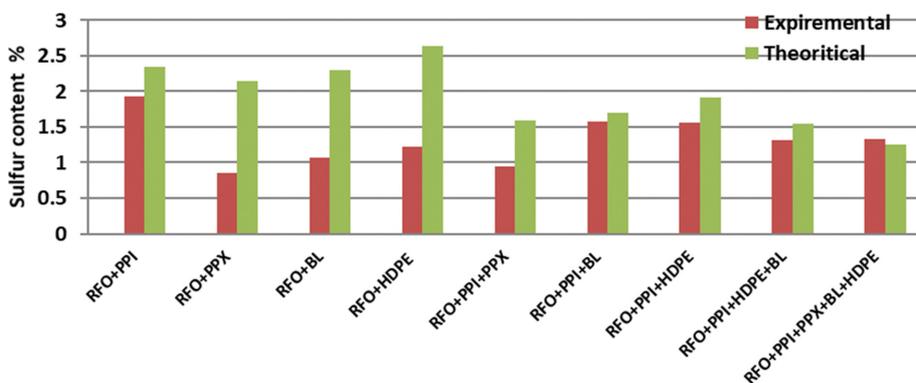


Fig. 8. Comparison of experimental and theoretical sulfur content of chars obtained from the co-cracking of RFO with various waste plastics.

tics is given in Fig. 5-9. From Fig. 5, the experimental carbon content is higher than that of the theoretical values except in the case of BL+HDPE and RFO+PPI+HDPE. However, in the case of hydrogen (Fig. 6), the theoretical values of hydrogen content are more or less equal or lower than that of the experimental values for the binary co-pyrolyzed char. The theoretical value of the hydrogen content of the char obtained from the ternary, quaternary, and quinary co-cracking is higher than that of the experimentally determined values. Fig. 7 shows that the binary co-pyrolyzed chars have higher theoretical values of nitrogen, and similar observations were made with the ternary mixture of RFO+PPI+PPX. While all the other

co-cracking processes, including ternary, quaternary and quinary, have lower theoretical values of nitrogen content in the char. The sulfur content shows higher theoretical values in all cases of mixture except in the case of quinary co-pyrolysis. However, on the contrary, in all combinations except PP+RFO and RFO+HDPE, the experimental value of oxygen content (%) was higher than that of the theoretical value. The above finding clearly proves that there was an interaction between the RFO and plastics during the co-cracking process. Fig. 8 shows that the experimental values of sulfur content in the char are higher than that of the theoretical values, clearly implying that co-cracking reduces the sulfur content in

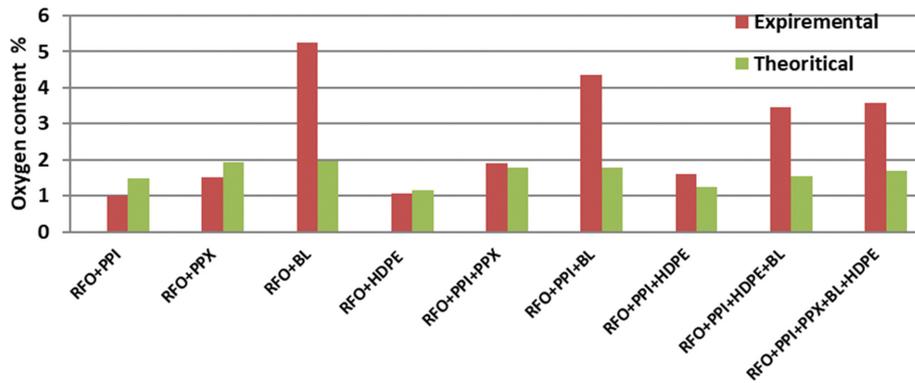


Fig. 9. Comparison of experimental and theoretical oxygen content of chars obtained from the co-cracking of RFO with various waste plastics.

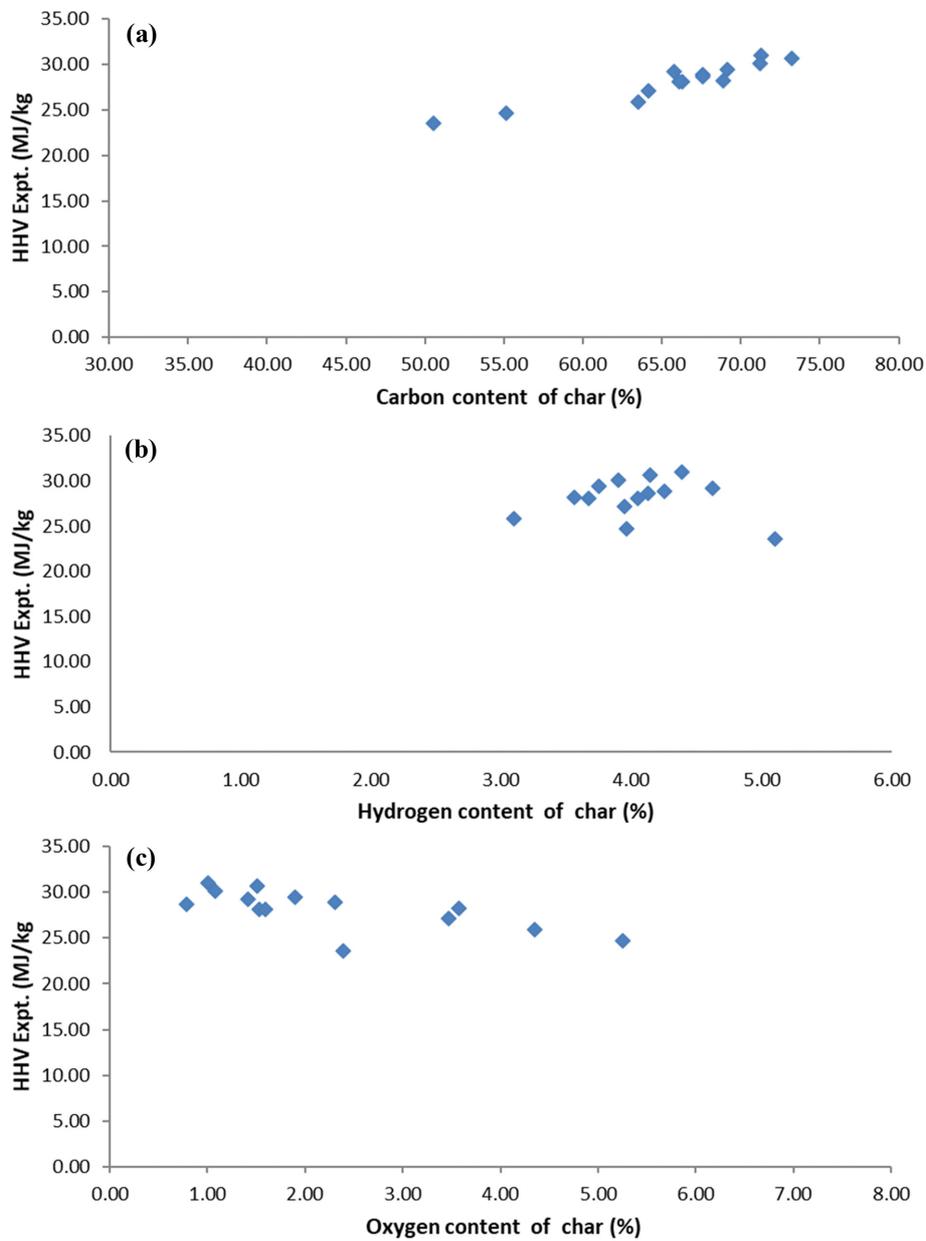


Fig. 10. Correlation between the ultimate analysis and HHV of char.

the char. However, the theoretical average values of oxygen of the char obtained from the co-cracking RFO+PPI and RFO+HDPE were higher than that of the experimental values (Fig. 9). Whereas, in all other combinations, the experimental values of oxygen content were higher than that of the theoretical values.

Fig. 10(a) demonstrates that with an increase in the content of carbon, the HHV also increases, and carbon being the primary constituent of the char it is apparent that the carbon content is responsible for the HHV of the char obtained from the co-cracking of plastics with RFO. Fig. 10(b) also shows that the overall impact of hydrogen content in the char has a positive contribution to the HHV of the char. However, the presence of oxygen, as shown in Fig. 10(c), decreases the HHV of the char, and therefore, the higher the content of oxygen in the char, the lower will be their HHV.

CONCLUSION

The char obtained from the ternary co-cracking of RFO+PPI+PPX, RFO+PPI+HDPE showed HHV of 29.46 and 28.12 MJ/kg, respectively. While the quaternary mixture of RFO+PPI+HDPE+BL showed HHV of 27.14 MJ/kg and the quinary mixture of RFO+PPI+PPX+BL+HDPE showed HHV of 28.20 MJ/kg. Among the proximate correlation models chosen for the prediction of HHV, Eq. (2) had the best agreement with the experimental values, with an R^2 value equal to 0.971, AAE, and ABE value of 1.70% and -0.68%, respectively. However, among the ultimate correlation models selected for the prediction of HHV of the char, Eq. (7) with R^2 of 0.98, AAE, and ABE of 0.37% and -2.46%, respectively, were found to be the best agreement with the experimental value. The chars obtained from the RFO, BL, HDPE, RFO+BL, and RFO+PPI+HDPE+BL are highly reactive and found to be more reactive than the rest of the mixture. Therefore, these chars have the potential and scope to be used for gasification as well as combustion. There is a significant increase in the experimental value compared to the theoretical value (taking the average of individuals) in the ash content of the char resulting from the co-cracking of RFO with BL, HDPE, PPI in binary, ternary, or quaternary mixture. Further, the experimental calorific values of the char resulting from the blended feedstocks are higher than that of the theoretical values. This shows that there was an explicit interaction between the co-feed materials during the co-cracking process, indicating a synergistic effect of blending. This is further an indication of diverse chemical reactions during the co-cracking process, resulting in the formation of liquid, solid, and gaseous products. From this study, it is concluded that the prediction of HHV from the correlation model using either the proximate or ultimate analysis data is reliable and rapid process of predicting HHV of char products. The fixed carbon, volatile matter, and carbon content are the major constituents of the char and are largely responsible for the calorific value of the char. This study has clearly shown that the char resulting from the co-cracking of waste plastics with RFO has a good calorific value. The carbon and hydrogen content of the char along with fixed carbon and volatile matter content are responsible for the calorific values of these chars. Further, the calorific values can be determined not only by conventional techniques but also by using predictive correlation models which are equally reliable yet

can be determined faster and easier once we know the proximate and ultimate characteristics of the char.

REFERENCES

1. M. Ahmaruzzaman, *Bioresour. Technol.*, **99**(11), 5043 (2008).
2. S. Biswas and D. K. Sharma, *J. Anal. Appl. Pyrolysis*, **101**, 17 (2013).
3. N. Phetyim and S. Pivsa-Art, *Energies*, **11**(11), 1 (2018).
4. J. G. Faillace, C. F. de Melo, S. P. L. de Souza and M. R. da Costa Marques, *J. Anal. Appl. Pyrolysis*, **126**, 70 (2017).
5. P. Kasar, D. K. Sharma and M. Ahmaruzzaman, *J. Clean. Prod.*, **265**, 121639 (2020).
6. P. Kasar and M. Ahmaruzzaman, *JSIR*, **78**, 426 (2019).
7. P. Kasar and M. Ahmaruzzaman, *Pet. Sci. Technol.*, **36**, 18 (2018).
8. V. K. Gupta and S. Sharma, *Ind. Eng. Chem. Res.*, **42**, 6619 (2003).
9. A. K. Jain, V. K. Gupta, A. Bhatnagar and S. Suhas, *J. Hazard. Mater.*, **101**, 31 (2003).
10. V. K. Gupta and I. Ali, *Colloid Interface Sci.*, **271**, 321 (2004).
11. S. A. Channiwala and P. P. Parikh, *Fuel*, **81**(8) 1051 (2002).
12. D. R. Nhuchhen and M. T. Afzal, *Bioengineering*, **4**(1) (2017).
13. C. Qian, Q. Li, Z. Zhang, X. Wang, J. Hu and W. Cao, *Fuel*, **265**, 116925 (2020).
14. T. Cordero, F. Marquez, J. Rodríguez-Mirasol, J. J. Rodriguez, *Fuel*, **80**, 1567 (2001).
15. S. Kucukbayrak, B. Durus, A. E. Mericboyu and E. Kadioglu, *Fuel*, **70**, 979 (1991).
16. P. Fernandez, R. M. Diaz and J. Xiberta, *Fuel*, **76**, 951 (1997).
17. A. Demirbas, *Fuel*, **76**, 431 (1997).
18. L. Jimenez and F. González, *Fuel*, **70**, 947 (1991).
19. K. Raveendran and A. Ganesh, *Fuel*, **75**, 1715 (1996).
20. D. W. van Krevelen and J. Schuyer, *Coal science- aspect of coal constitution*, Amsterdam: Elsevier Pub. Co (1957).
21. ASTM D 3172-73(84), Standards method of proximate analysis of coal and coke in gaseous fuels; coal and coke, 1989, p. 299.
22. ASTM D 3175-89, Standards test method for volatile matter in the analysis sample of coal and coke, in gaseous fuels; coal and coke, 1989, p. 305.
23. ASTM D 3173-87, Standards test method for moisture in the analysis sample of coal and coke, in gaseous fuels; coal and coke, 1989, p. 300.
24. ASTM D 3174-89, Standards test method for ash in the analysis sample of coal and coke, in gaseous fuels; coal and coke, 1989, p. 302.
25. D. R. Nhuchhen and P. Abdul Salam, *Fuel*, **99**, 55 (2012).
26. D. R. Nhuchhen, *Fuel*, **180**, 348 (2016).
27. J. Parikh, S. A. Channiwala and G. K. Ghosal, *Fuel*, **84**, 487 (2005).
28. W. A. Selvig and F. H. Gibson, *Calorific value of coal*, 1st Ed. New York, Wiley (1945).
29. W. Boie, *Energietechnik*, **3**, 309 (1953).
30. K. Miura, M. Makino and P. Silveston, *Fuel*, **69**, 580 (1990).
31. H. Darmstadt, C. Roy, S. Kaliaguine and H. Corner, *Rubber Chem. Technol.*, **70**, 759 (1997).
32. I. Boumanchar, Y. Chhiti, F. E. M'thamdi Alaoui, A. Sahibed-Dine, F. Bentiss, C. Jama and M. Bensitel, *Waste Manag. Res.*, **37**(6), 578 (2019).
33. L. Ballice, *Fuel*, **81**, 1233 (2002).