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Research Article

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Posted Date: June 8th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-256550/v1>

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Utilization of Refuse Derived Fuel for Energy Recovery Processes: Prediction of Environmental Emissions and Thermal Behaviour in Combustion Processes

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ABSTRACT

In the present study, the environmental emissions from co-combustion of refuse derived fuel (RDF) in cement plants and coal-fired power plants are predicted using mass and energy flow modeling. Mumbai was considered as study area and RDF characteristics were assessed using MSW composition in Mumbai. The modeling results suggested that with increase in RDF share in fuel mixture, significant reduction in environmental parameters such as winter smog, global warming and acidification potentials could be achieved, though the electricity and heat generation were reduced. This problem can be overcome by improving the quality of RDF. Moreover, thermal gravimetric analysis (TGA) of individual RDF components (compostable organic matter, paper, wood and plastic) was carried out in oxidative environment to understand their thermal stability. Average activation energies for plastic, wood and compostable organics (98.6-183 kJ/mol) were comparable to those reported for coal. The results suggest that coal and

RDF co-combustion should not affect the combustion profile. Moreover, high plastic content in RDF can assist in control of combustion process and also can enhance its calorific value.

Keywords: Energy recovery; Mass and energy flow modeling; Municipal solid waste; Refuse derived fuel; Thermogravimetric analysis

Acknowledgements

First two authors, Mr. Deepak Kumar Singhal and Ms. Divya Gupta, are thankful to Ministry of Human Resource Development, Government of India for providing fellowship to conduct this research study.

Declarations

Funding: None

Conflicts of interest/Competing interests: The authors declare that they have no conflict of interest.

Availability of data and material: None

Code availability: None

Authors' contributions: Conceptualization: Prof. Anurag Garg and Mr. Deepak Kumar Singhal; Material preparation, data collection and initial analysis: Mr. Deepak Kumar Singhal; Detailed analysis and interpretation of results: Mr. Deepak Kumar Singhal and Ms. Divya Gupta; Writing - Original draft preparation: Mr. Deepak Kumar Singhal and Ms. Divya Gupta; Writing – Review and editing: Prof. Anurag Garg; Supervision: Prof. Anurag Garg. Read and approval: All authors

1. Introduction

The level of industrialization, urbanization and population dictates the municipal solid waste (MSW) generation and its composition at a particular place. With increase in economic status of a country, the amount of combustible fraction in MSW is likely to increase. For example, the paper, plastic and rubber contents increased from 4.72% (year 1996) to 17.35% (year 2005) in India (Central Public Health and Environmental Engineering Organization (CPHEEO), 2016). Although waste-to-energy (WtE) is the penultimate option in waste hierarchy, it is recognized a potential option for disposal of the combustible MSW fraction (Psomopoulos et al., 2009; United States Environmental Protection Agency (USEPA), 2009). The utilization of refuse derived fuel (RDF), obtained from MSW, as co-fuel in energy intensive industries (e.g., cement kilns and coal-fired power plants) will mitigate the concerns over the shortage of fossil fuels globally. Meanwhile, the presence of significant biogenic fraction (wood, paper, textile etc.) may help in earning carbon credits by lowering greenhouse gas (GHG) emissions due to biogenic fraction of the waste (Georgiopoulou and Lyberatos, 2018). Nevertheless, the industries (particularly in developing countries) still have reservations about RDF performance in combustion systems as co-fuel and environmental emissions. Hence, the present study examines the environmental performance of RDF as co-fuel for energy recovery purposes. Moreover, the thermal behavior of major RDF constituents during combustion process is also reported.

Cement production is an energy intensive process contributing ~8% of the global CO₂ emissions from anthropogenic sources (Georgiopoulou and Lyberatos, 2018). Several studies have been performed on the estimation of energy generation and emissions from the various waste to energy options in European countries mainly due to increased regulatory pressure (Garg et al., 2007; Garg et al., 2009; Georgiopoulou and Lyberatos, 2018; Mari et al., 2018). Since MSW

composition and constituents in the developing countries are very different from that generated in European or other developed countries, the similar estimates need to be made for assessing the production of useful heat/ energy and environmental emissions.

Using RDF as co-fuel may be less expensive in comparison to building a dedicated MSW or RDF incineration facility (Ouda et al., 2016). Havukainen et al. (2017) reported that the incineration of MSW derived RDF along with electricity production could lead to maximum reduction in global warming, acidification and eutrophication potentials as compared to direct landfilling and incineration of MSW in China. In another study, from China, a reduction of 46,144 tonnes of CO₂ eq emissions from a cement plant was reported due to the use of RDF as co-fuel with coal (Wang, 2017). Reymond et al. (2018) conducted efficiency analysis of alternative fuel technology for GHG reduction in a cement industry (production capacity = 7100 tonnes/d). They reported higher carbon emissions (~47 ton CO₂/year) from coal burning in a cement plant compared to ~30 ton CO₂/year from the same amount of RDF. Tiwary et al. (2014) performed trial co-combustion runs with different hazardous and non-hazardous wastes to monitor gaseous releases from 21 cement plants located in India. Most of the parameters such as particulate matter, polycyclic aromatic hydrocarbons, NO_x, CO, HCl, and volatile organic carbon were found to reduce during co-combustion with no compromise with the clinker quality. Along with reduction in amount of coal used and CO₂ emitted, significant landfill volume saving could also be achieved.

Though some interesting and encouraging studies are available on cement plants, there is a need to perform mass and energy flow analysis to gain more insight about RDF utilization not only in cement plants but also in other potential outlets such as coal-fired power plants. Moreover, thermal stability of RDF components needs to be examined in lab scale combustion studies

which should be useful to find kinetic parameters. Mass and energy flow modeling is relatively a cost-effective method compared to establishing an expensive pilot plant in the beginning. Based on modeling and lab scale kinetic results, pilot scale studies should be planned in the next phase.

Hence, the present study was undertaken to predict the effect on electricity generation/ heat recovery potential and environmental emissions from the utilization of RDF as co-fuel in cement and coal-fired power plants using a modular mass and energy flow model. Mumbai was selected as the study area since urban cities are facing tremendous pressure due to shortage of sufficient land for waste landfilling. Moreover, Solid Waste Management (SWM) Rules (2016), encourage RDF production and its co-combustion in energy intensive industries to increase MSW diversion from landfills. According to the published data, MSW generation in Mumbai is 9645 tonnes/d (excluding ~2000 t/d from construction and demolition activities) (Annepu, 2011). Apart from this, thermal behavior of various RDF components was studied in oxidative environment through thermal gravimetric analysis (TGA). The obtained data was used to determine the kinetic constants using iso-conversional modeling approach.

2. Methodology

2.1. Refuse derived fuel composition and characteristics

RDF composition in Mumbai was predicted using the waste sorting scheme proposed by Nithikul et al. (2011). The detailed methodology used to predict RDF composition and characteristics from MSW generated from Mumbai has been reported elsewhere (Singhal and Garg, 2015). It was predicted that ~23% RDF can be produced after mechanical sorting of mixed MSW. In summary, RDF contains ~35% (by weight) biogenic materials (paper, compostables, wood and textile), 35.5% plastic and ~28% miscellaneous components. Organic compostable waste mainly comprised of food and yard wastes while plastics fraction is generally composed of

polyethylene, polypropylene, polyvinyl chloride (PVC), polystyrene and polyethylene tetra phthalate (PET). The moisture content, higher heating value and lower heating values were estimated as 25.5%, ~17 MJ/kg and ~11 MJ/kg.

2.2. RDF co-combustion scenarios

In this study, five co-combustion scenarios for RDF utilization in cement and power industry were considered (located within 200 km from Mumbai) (Singhal and Garg, 2015). The performance of these co-combustion scenarios was compared with conventional coal combustion scenarios in both cement kiln and power plant (i.e., scenarios 1 and 5). The share of RDF in input fuel and its feed rate for various scenarios is presented in Table 1.

Table 1. Summary of the scenarios modeled

RDF outlets	Cement kiln (1 Mt/y)				Power plant (2780 MW)		
Scenario Number	1	2	3	4	5	6	7
Share of RDF (by weight)	0%	25%	30%	40%	0%	4%	4.5%
Coal feed rate (kg/h)	25047	18785	17533	15028	190121	182516	1815661
RDF feed rate (kg/h)	0	6262	7514	10019	0	76049	85555

2.3. Mass and energy flow modeling framework

In this study, a simple mass and energy flow model earlier used for the utilization of solid recovered fuel (SRF) and sewage biosolids as co-fuel was modified by including transportation as an activity (Cartmell et al., 2006; Garg et al., 2009). The model features a series of modules such as fuel combustion chamber, gas cleaning devices like particulate removal unit and absorption tower, heat exchanger to produce steam from steam turbine, to predict the final emissions and energy output (Fig. 1).

The input data required for the modified mass and energy flow model include fuel and air feed rate, moisture content, ash content, elemental composition (C, H, O, N, S and Cl) and heating values for both fuels (i.e., coal and RDF). Coal and MSW derived RDF characteristics are provided in Supplementary Information (Table S1).

Following assumptions were made to perform energy and mass balance calculations:

- i) The oxygen requirement was calculated using the elemental analysis of the feed. This was then used to determine the stoichiometric air (composed of 79% nitrogen and 21% oxygen by volume) requirement.
- ii) To ensure complete combustion, 30% (w/w) excess air was supplied to the combustion facility.
- iii) Complete conversion of Cl to HCl was assumed to occur during combustion. Besides, 99% of combustible sulphur is supposed to be converted into SO₂ and remaining 1% is converted into SO₃ (Mycock et al., 1995).
- iv) Temperature of the combustion chamber was maintained above 850°C to eliminate emissions of dioxins, furans and other volatile organic compounds
- v) Above 1000°C combustion leads to the formation of NO_x in the flue gas stream (Tchobanoglous et al., 2015). At lower combustion temperatures, it has been roughly assumed that 6% (w/w) nitrogen from fuel mixture will be converted into NO and N₂O in equal proportion (1:1) (Cartmell et al., 2006).
- vi) Ash component generally contains 5% (w/w) unburnt carbon (Tchobanoglous et al., 2015). Furthermore, it was assumed that fly ash constitutes 15% (w/w) of the total ash content while the remaining (i.e., 85%) is bottom ash (Sabbas et al., 2003).

- vii) Radiation loss in the boiler was assumed 0.5% of the total heat input (Tchobanoglous et al., 2015).
- viii) Temperature of the hot flue gas stream was reduced to 150°C after coming out of combustion chamber to reduce the volume of gas and to protect the downstream control devices (Tchobanoglous et al., 2015).
- ix) Efficiencies of the combined heat exchange/steam turbine and generator were taken as 35% and 99%, respectively, when RDF was co-combusted for electricity generation purposes. In cement kilns, only 50% heat was assumed to be available for the combined heat and power (CHP) unit (Garg et al., 2007).
- x) It is assumed that only the heavy commercial vehicles will be used for the transportation of RDF from material recovery facility to the industry or energy recovery facility and hence the emission factors prescribed by Bharat Stage II (BS II) emission standards for such vehicles were used to determine the emissions (HC, CO, NO_x, and particulate matter) during fuel transportation (URL-01).

Model output data was used to determine the environmental impacts and electricity or heat generation. Several parameters like CO₂, HCl, NO_x, SO₂, SO₃ and fly ash (kg/h) were used to assess global warming, acidification and winter smog potentials. Using Ecoindicator 95 data (Goedkoop and Spriensma, 2001), the following equations were used for determining these potentials:

$$\text{Global warming potential (in kg CO}_2\text{ equiv./h)} = \text{CO}_2\text{ (kg/h)} + \text{N}_2\text{O (kg/h)} * 270 \quad (1)$$

$$\text{Acidification potential (in kg SO}_2\text{ equiv./h)} = \text{NO}_x\text{ (kg/h)} * 0.7 + \text{HCl (kg/h)} * 0.88 + \text{SO}_2\text{ (kg/h)} \quad (2)$$

$$\text{Winter smog potential} = \text{dust (kg/h)} + \text{SO}_2 \text{ (kg/h)} \text{ in kg dust/h} \quad (3)$$

Eventually, a comparison was made between coal mono-combustion and co-combustion scenarios.

Insert Fig. 1 here

2.4. Combustion experiments at laboratory scale and kinetic study

Oven-dried individual MSW components (such as compostable organics, wood, paper and plastic waste) were subjected to the thermal analysis for prediction of their behavior during combustion. The combustion experiments were carried out in a Shimadzu DTG-60/60H TGA unit. A known amount of dried and ground individual sample (~14-15 mg) was taken on a platinum pan. The sample was heated up to 900°C in an oxidizing atmosphere using air (flow rate = 100 mL/min). The sample heating rate was varied from 10°C/min to 50°C/min. The thermogravimetric (TG) and differential thermogravimetric (DTG) data obtained from the runs for different MSW components were plotted against temperature to understand the thermal degradation pattern, and overall mass loss.

In the present study, isoconversional (i.e., model-free) approach was used to determine kinetic parameters (Vyazovkin and Wight, 1998; Yanfen and Xiaoqian, 2010). Using this approach, the intrinsic reaction rate coefficients were obtained for the combustion of individual MSW components under differential oxidizing conditions. To determine the kinetic parameters (such as rate constant and activation energy), the non-isothermal TG data was fitted into the model. It calculates the activation energy (E) of the process using dynamic integral TG curves obtained with at least three different heating rates (β).

The rate of heterogeneous solid-state reactions can generally be expressed as follows:

$$\frac{d\alpha}{dt} = k(T).f(\alpha) \quad (4)$$

where, t = time; $k(T)$ = temperature-dependent constant, $f(\alpha)$ = a function which describes dependency of the reaction rate on the extent of reaction, α .

The temperature dependence of rate constant is described by Arrhenius equation. Thus, the final rate of a solid-state reaction can be described by equation 5:

$$\frac{d\alpha}{dt} = A e^{-E/R.T}.f(\alpha) \quad (5)$$

where, A = pre-exponential Arrhenius factor; E = activation energy; R = universal gas constant
Since the data was obtained at a constant heating rate (β), this term was introduced in equation (5) and the above rate expression was transformed into non-isothermal rate expression (equation 6) which was as follows:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} A.e^{(-E/R.T)}.f(\alpha) \quad (6)$$

Upon integrating equation (6) from 0 to α (i.e., extent of fuel conversion), the following expression is obtained:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-E/R.T} dT \quad (7)$$

Since $2RT/E \ll 1$, the temperature integral can be simplified further:

$$g(\alpha) = \frac{A.R}{\beta E} .T^2 .e^{-E/R.T} \quad (8)$$

Rearranging and taking the logarithm, equation 8 can be written as

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{R.A}{E.g(\alpha)}\right] - \frac{E}{R.T} \quad (9)$$

For each conversion value (i.e., α), $\ln (\beta/T^2)$ versus $1/T$ was plotted which will give a straight line with slope $-E/R$. Therefore, E value is obtained as a function of the conversion.

In order to determine the order of reaction, variation in the degree of fuel conversion with temperature and heating rate is expressed as equation 10.

$$\alpha(T) = 1 - \exp\left[-\frac{k(T)}{\beta^n}\right] \quad (10)$$

Substituting $k(T) = A.e^{-E/R.T}$ in the above equation and taking the double logarithm of both sides, the following expression is obtained:

$$\ln[-\ln(1 - \alpha(T))] = \ln A - \frac{E}{R.T} - n.\ln \beta \quad (11)$$

Hence, a plot between $\ln[-\ln(1 - \alpha(T))]$ and $\ln \beta$ at a particular temperature from number of isotherms taken at different heating rates provides straight lines. The slope of these lines is the order of reaction. An overall reaction order can be obtained after taking average of reaction orders obtained at different temperatures.

3. Results and Discussion

3.1. Mass and energy flow model

Using the modeling results, the impacts on electricity generation/ heat recovery, air emissions and ash production were assessed. As an example, the mass and energy flow diagram for scenario 2 is shown in Fig. 2. The flow diagrams for the remaining scenarios are provided in supporting information (Fig. S1-S6 in Supplementary Information).

Cement industry

For a cement industry located in Raigad (around 36 km from Mumbai), three different combinations of RDF and coal as feed were modeled (Table 1). The results suggested the

decrease in CO₂, NO_x and SO_x by 8-13%, 16-24% and 13-20.5%, respectively if 25-40% of the coal is replaced by RDF. Moreover, the ash emissions were also reduced by 11-18%. By RDF substitution of 7-75.5% in cement industries, a reduction of 2.5-27.2% in CO₂ emissions has been reported previously (Schwarzböck et al., 2016). Additional GHG savings of 6.3 million tons CO₂-equivalents per year were also reported due to diversion of waste from landfills in Indonesian cement industries. In another study, Genon and Brizio (2008) reported a reduction in CO₂ and NO_x of 1.61 kg/kg RDF and 0.36 kg /t RDF, respectively in comparison to that with coal. Lower nitrogen concentration in RDF (0.4%) as compared to 1.2% in coal could reduce NO_x emissions (Table S1 in Supplementary Information). However, HCl emissions were ~5.5-9.0 times to that obtained from scenario 1 (i.e., coal mono-combustion) with increase of RDF in the feed primarily due to high Cl content in the waste derived fuel which is also reported earlier (Reza et al., 2013). The gaseous (CO and HC) and particulate (PM) emissions during fuel (coal and RDF) transportation were reduced by 13%, 15% and 19% by increasing RDF share in the input fuel due to the following two reasons: (i) the source of coal is located farther away compared to RDF production plant, and (ii) number of trips to the coal site was reduced due to its lesser demand.

Power industry

There are three power industries (total capacity = 2780 MW) located within 200 km distance from Mumbai. In power industries, the maximum RDF share of the total power plant fuel feed) can be only 4.5% which is equivalent to the total RDF production. Therefore, the mass and energy flow modeling was performed for two coal and RDF mixtures (i.e., 4 and 4.5%). The results were compared with the mono-combustion of coal (scenario 5). The analysis showed a significant reduction in environmental emissions though the electricity production also decreased

by 33 MW with 4.5% RDF. CO₂ emissions (including during transportation) could be reduced by ~1% and 2% when RDF was 4 and 4.5%, respectively, in the fuel. Similarly, NO_x emissions were reduced by 2% and 3% for RDF share of 4 and 4.5%, in the fuel respectively. Same trends were also observed for SO_x reduction (2 and 2.3%) and ash content (~2%) for both the combinations of coal and RDF. Again, an increase in HCl emissions was found.

Insert Fig. 2 here.

The individual gaseous and particulate emissions in flue gas for different scenarios are presented in Table 2. The analysis predicted that CO₂ emissions from co-combustion scenarios can be reduced by ~40 tonnes/h even if only 4-4.5% RDF is used in fuel mixture which is a significant reduction. However, HCl emissions significantly increased for co-combustion in cement and power plants (upto ~9 and 2 times, respectively). High chlorine content in fuel mixture is undesirable as it can corrode combustor wall and other accessories. To suppress its emissions, polyvinyl chloride (PVC) as well as compostable organic fraction (particularly food waste) should be segregated. Use of salt (i.e., NaCl) is the source of chlorine in food waste fraction. As an alternative, biodrying may be adopted to reduce moisture content in the mixed waste which will eventually improve efficiency of waste sorting units. Moreover, heating value of RDF will also improve significantly.

It should be noted that the environmental indicators such as global warming, acidification and winter smog were reduced significantly when a mixture of coal and RDF was burned (Fig. 3). Though a reduction in heat or electricity generation was seen in co-combustion scenarios. The reductions in the product and environmental emissions was higher for scenarios 6 & 7 associated with coal-fired power plants. This is due to the higher amount of coal replaced by RDF in power plants. To compensate heat or electricity loss, the industries can use alternative co-fuel (such as

wood) with coal and RDF. As it is stated in previous paragraph, the improved sorting can enhance heating value of waste derived material comparable to that of Indian coal.

Table 2. Comparison of different scenarios with respect to emissions

Air emissions	RDF in fuel mixture (%)						
	Cement Industry				Power Industry		
	Scenario	Scenario	Scenario	Scenario	Scenario	Scenario	Scenario
	1 0%	2 25%	3 30%	4 40%	5 0%	6 4%	7 4.5%
Net CO ₂ (kg/h)	37535	34378	33752	32511	2847665	2809514	2804692
SO ₂ (kg/h)	1.00	0.87	0.84	0.79	75.7	74.2	74.0
SO ₃ (kg/h)	0.013	0.011	0.011	0.010	0.96	0.94	0.93
Net SO _x (kg/h)	1.01	0.88	0.85	0.80	76.7	75.1	74.9
NO (kg/h)	19.6	16.3	15.6	14.3	1491.1	1450.5	1445.4
N ₂ O (kg/h)	14.4	12.0	11.5	10.5	1093.5	1063.7	1060.0
Net NO _x (kg/h)	54.4	45.9	44.3	41.2	4110.9	4010.5	3997.3
HCl (kg/h)	0.22	1.4	1.7	2.2	16.6	31.3	33.1
CO (kg/h)	13.1	11.4	11.1	10.6	984.8	965.3	962.5
HC (kg/h)	0.81	0.70	0.68	0.65	60.73	59.53	59.35
Ash content in flue gas (kg/h)	8.7	7.74	7.5	7.2	661	649	648
PM (kg/h)	2.7	2.4	2.3	2.2	203.5	199.5	198.9

Insert Fig. 3 here.

3.2. Results from thermogravimetric analysis of RDF constituents

3.2.1. Thermal behavior of individual waste components

TG analysis was performed in oxidizing atmosphere (air flow rate = 100 ml/min) for four major MSW components (compostable organic, wood, paper and plastic) amounting to more than 80% of the total MSW in Mumbai. The TGA mass loss and DTG curves are shown in Figures S7 and S8 (Supplementary Information), respectively.

The TG and DTG curves for biogenic fractions (i.e., compostable organic matter, wood and paper wastes) followed similar patterns whereas the curves for plastic waste were distinctly different. From the biomass derived materials, the mass loss due to release of moisture (upto 150°C) was ~6-10% at different heating rates though no loss in mass was observed from plastic samples (Fig. S7 in Supplementary Information). Although the samples were oven dried, the reason for reduction in mass for biogenic fractions can be the release of bound water present in the pores. In comparison, plastic is hydrophobic in nature and its moisture absorption capacity is very low. The moisture loss was followed by combustion of organic matter present in the sample which resulted in significant mass loss in all the four samples and the final mass was ~5-10% of the initial mass. The TG curves exhibited consistent sharp mass reduction (start and end temperatures = ~225-250°C and ~450-650°C, respectively). Though, two distinct peaks can be observed in the DTG curves for the biomass derived materials in contrast to one broad peak (at heating rate of 50°C/min) and two overlapping peaks (at 10 and 25°C/min heating rates) in the curves for plastic (Fig. S8 in Supplementary Information). In the DTG curves for biomass and its derivatives, the first prominent peak in rapid mass loss zone largely showed the removal of hemi-cellulosic matter (start range = ~225-250°C and end range = ~375-400°C) while the following second peak could be assigned to the removal of lignin type compounds (~400-675°C). The highest degradation temperature was observed for compostable organic waste and wood as the former may contain yard waste (such as plants, leaves etc.) while lignin is one of the major compound found in wood. Since lignin is separated by pulping process during paper manufacturing from woody biomass, it is likely to contain much lower lignin. Hence, its end temperature was lower. It has been well reported that lignin degradation temperature is higher than hemi-cellulosic matter (Cheng et al., 2012). However, the temperature range will also be

affected by the fuel heating rate and it was generally narrower for the runs with lower heating rate. Furthermore, the mass loss rate enhanced with increase in heating rate since the residence time for combustion is higher for low heating rate runs. The highest mass loss rates for compostable organic matter, wood and paper were 1.8, 1.05 and 1.3%/min, respectively at 50°C/min heating rate whereas the corresponding lowest mass loss rates were 0.2, 0.1 and 0.1%/min at a heating rate of 10°C/min (Fig. S8 in Supplementary Information). Similar results for different waste fractions (i.e., wood, cardboard and mixed waste) were observed by Kple et al. (2016). The maximum mass loss rate during combustion was in the range of 230-330°C with the second peak was found between 350°C and 500°C at 10°C/min heating rate.

In contrast, the rapid degradation of plastic waste leading to almost complete combustion occurred between 240°C to 490°C temperature (Fig. S7d in Supplementary Information) which is similar to that reported for polythene (240-415°C) and polystyrene (250-400°C) (Peterson et al., 2001). Since, plastic is manufactured using petrochemicals which are likely to be degraded faster, distinct peaks could not be observed at any heating rate though some degree of separation in peaks was seen in the DTG curve at lower heating rate (Fig. S8d in Supplementary Information). For plastic, the maximum and minimum mass loss rates were 0.6%/min and 0.2%/min, respectively at 50°C/min and 10°C/min heating rates.

The maximum loss in mass of plastic occurred at ~440°C compared to ~340°C for other components. This can be inferred that lower volatile fraction was present in plastic. High volatile matter in fuel can aid in reducing the ignition temperature but it may also lead to uncontrolled combustion and black smoke. It is evident from DTG curves that MSW components started release of volatile matter at 250-300°C temperatures which is comparable to the temperature for

coal samples from different countries (Muthuraman et al., 2010). Having higher plastic in RDF may support the controlled co-combustion.

3.2.2. Determination of activation energy for combustion

The method for determining activation energy has been described in section 2.4. The activation energy was determined using equation 9 and plotting between $\ln(\beta/T^2)$ versus $1/T$ for different heating rates at a particular conversion (i.e., α). The value of α was varied from 10-70% for wood and biomass derived materials while for plastic, it was 10-90%. The best fit straight lines for various components are illustrated in Fig. 4. The slope of these straight lines (i.e., $-E/R$) was used to calculate activation energy for each conversion value while arithmetic mean was taken to find average activation energy for each component (Table 3).

The average activation energy for the combustion of paper was lowest (i.e., ~ 98.6 kJ/mol) among all the materials. For other materials, i.e., wood, compostable organic waste and plastic, it was ~ 134 , ~ 162 and ~ 183 kJ/mol). This should be noted that the activation energy was increased upto 50% consistently (for compostable organic matter and wood) however the increase in activation energy was much higher for conversion of 60% in case of all materials. Subsequently, the activation energy dropped drastically for wood and biomass derived materials though it still increased for plastic samples upto 80% conversion. The complex compounds will require more energy for degradation. The combustion of volatile matter is comparatively easier and requires lesser energy than that needed for complex organics like lignin. Once lignin is broken down into simpler compounds, the activation energy may be reduced. Therefore, a reduction in activation energy was observed for biomass materials.

Table 3. Estimated activation energy for combustion of MSW constituents

Waste	Conversion (%)	Slope	E (kJ/mol)	Average E (kJ/mol)
Compostable organic matter	10	-13.09	108.78	161.8
	20	-14.38	119.50	
	30	-18	149.58	
	40	-19.9	165.37	
	50	-23.35	194.04	
	60	-32.41	269.33	
	70	-15.18	126.15	
Wood	10	-4.152	34.50	133.78
	20	-11.33	94.15	
	30	-13.51	112.27	
	40	-16.62	138.11	
	50	-19.65	163.29	
	60	-29.84	247.97	
	70	-17.59	146.17	
Paper	10	-9.694	80.56	98.58
	20	-10.34	85.93	
	30	-10.24	85.09	
	40	-10.11	84.01	
	50	-13.55	112.60	
	60	-19.5	162.05	
	70	-9.61	79.86	
Plastic	10	-9.882	82.12	182.93
	20	-11.89	98.81	
	30	-11.87	98.64	
	40	-14.09	117.09	
	50	-18.6	154.57	
	60	-30.84	256.28	
	70	-39.9	331.57	
	80	-41.38	343.87	
	90	-19.67	163.46	

The activation energies obtained in the present study matches with those reported in literature. For instance, this can be 69-217 kJ/mol and 123-136 kJ/mol combustion of paper sludge and untreated wood, respectively (Yorulmaz and Atimtay, 2009; Yanfen and Xiaoqian, 2010). High activation energy of plastic indicates the presence of substantial amount of polythene. Activation energy of high density polyethylene (HDPE) was estimated as ~172 kJ/mol (Al-Salem et al., 2010) whereas Gao et al. (2003) have reported the activation energy range of 160-320 kJ/mol for polyethylene. Ignition temperatures of Indian, Australian and Indonesian coals are reported to be 398°C, 471°C and 418°C respectively while the activation energy for combustion of various coals are ~119 kJ/mol, ~170 kJ/mol and ~152 kJ/mol, respectively (Muthuraman et al., 2010) which are in agreement to those obtained in present study. Hence, this can be suggested that RDF co-combustion with coal will not affect the combustion profile significantly.

Insert Fig. 4 here.

3.2.3. Determination of combustion reaction order for various MSW constituents

For the computation of reaction order for various components, the curves were plotted for each MSW component between 27°C to 927°C. At each of these temperatures, the conversion (α) was determined for each heating rate (β) and the curves were plotted between $\ln[-\ln(1-\alpha(T))]$ vs $\ln \beta$ (as per equation 11). The slope of these curves represents the reaction order (n) at a particular temperature (Fig. 5). The reaction order for compostable organic waste, wood, paper and plastic are presented as a function of temperature in Table 4. The average order of reaction for compostable organic waste was the lowest (= 0.12) and it was highest (= 0.47) for the plastic sample. The reaction order for wood and paper wastes were almost similar ~0.30. The individual reaction orders were ranged from 0.01 (pseudo zero-order reaction) to 0.6 showing their dependency on the extent of the reaction i.e., not constant during the reaction.

Insert Fig. 5 here.

Table 4. Reaction order for different waste components

Temperature (°C)	Reaction Order (n)			
	Organic compostable	Wood	Paper	Plastic
200	0.01	0.94	0.16	0.36
250	0.12	0.35	0.34	0.47
300	0.37	0.33	0.60	0.55
350	0.08	0.17	0.36	0.57
400	0.05	0.03	0.12	0.54
450	0.08	0.05	0.15	0.32
Average n	0.12	0.31	0.29	0.47

4. Conclusions

MSW derived RDF can be used as a co-fuel in energy intensive industries such as cement kilns and coal fired power plants. Use of RDF as co-fuel resulted in decrease of gaseous and particulate emissions (CO_2 , SO_x , NO_x and PM) with increase in RDF content. As a result, there were significant reductions in winter smog (13-19% for cement industry and 2-2.3% for power industry), global warming (9-14% for cement industry, 1.5-1.7% for power industry) and acidification (12.7-19.8% for cement industry, 2.0-2.3% for power industry) potentials. However, increased RDF to fuel ratio can reduce electricity and heat generation due to lower calorific value. To compensate this loss, RDF quality needs to be raised by adopting improved strategy for waste segregation. This may be accomplished by source segregation and/ or

biodrying of mixed MSW to strike off the moisture so that the performance of downstream mechanical units is enhanced.

TGA-DTG analysis results revealed that the combustion profiles for biogenic fractions were very different from plastic which had lower volatile matter, highest activation energy (= 183 kJ/mol) and higher mass loss temperature. Thus, higher plastic content in RDF is desirable to control combustion of RDF and coal mixture. Average activation energies and volatile release temperatures for plastic, wood and compostable organics were comparable to those for different types of coals. Hence, coal and RDF co-combustion is not likely to influence the combustion profile. To validate the modeling results, pilot scale studies for MSW segregation and its co-combustion in energy intensive industries should be performed. Detailed economic analysis of MSW treatment to prepare RDF must be performed.

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Figure Captions

Fig.1 Framework mass and energy flow model configured for (a) electricity generation and (b) combined heat and power

Fig.2 Mass and energy flow balance for scenario 2 (coal + 25% RDF in cement kiln)

Fig.3 Effect of different scenarios on: (a) change in electricity generation/ heat supplied, (b) global warming potential, (c) acidification potential, and (d) winter smog potential

Fig.4 Determination of activation energy (E) using model free approach: (a) compostable organic matter, (b) wood, (c) paper and (d) plastic

Fig.5 Determination of order of reaction (n) using model free approach: (a) compostable organic matter, (b) wood, (c) paper and (d) plastic

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

MSW

Refuse derived fuel

- Wood
- Plastic
- Paper
- Compostable organic matter

Thermal behaviour and combustion kinetics

TGA curve for combustion of compostable organic matter

Reduction in Global Warming potential (kg CO₂/h)

	Activation energy (kJ/mol)	Reaction order
Wood	133.78	0.31
Plastic	182.93	0.47
Paper	98.58	0.29
Compostable organic matter	161.80	0.12

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