Indonesian Journal of Environmental Management and Sustainability
e-ISSN:2598-6279 p-ISSN:2598-6260

Research Paper

Emission and Heavy Metal Content Characteristic of Densified Refused Derived Fuels of Oil Sludge and Biomass Combination as an Alternative Fuel for Cement Plant

Rati Yuliarningsih[1]*, Fadjar Goembira[1], Puti Sri Komala[1], Nino Perdana Putra[2]

[1]*Master Program of Environmental Engineering, Universitas Andalas, Padang-West Sumatera, Indonesia*
[2]*Clinker Production Department, Semen Padang, Padang-West Sumatera, Indonesia*
***Corresponding author e-mail**: ratiyuliarningsih12@gmail.com

Abstract
Hazardous Waste such Oil Sludge combined with biomass (coconut shell and rice husk) was utilized as an alternative fuel in cement plant in form of Densified-Refused Derived Fuel (D-RDF). D-RDF were Co-Processed with primary fuel into Rotary Kiln in order to reduce usage of fossil fuel and eliminate the hazardous waste by thermal treatment, meanwhile to recover the energy contained in the D-RDF, the utilization of these waste are expected without causing adverse effect into the environment. Co-Processing of D-RDF as alternative fuels into cement plant kiln must follow the regulation applied in Indonesian Environment and Forestry Minister regulation 19/2017 and European Union for Responsible Incineration and Treatment of Special Waste (EURITS). Based on previous research, D-RDF composition of oil sludge and biomass at 1:1 ratio with 5% starch addition was choose as they give best calorific value at 6000 kcal/kg. The objectives of this research are to observe the emission caused by the utilization of these D-RDF and potential effect into cement or clinker product. The result show NOx and CO value are meet the standard requirement by government regulation meanwhile SO_2 value which are 1251 mg/Nm^3 and 1500 mg/Nm^3, over the regulation standard which is 650 mg/Nm^3. This issue could be overcome in the plant with pretreatment of D-RDF and utilization of Bag House Filter or Electrostatic Precipitator before release the emission to the stack. Trace element analysis of D-RDF ashes (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Se, Sn dan Zn) show the result are meet the EURITS regulation, which mean utilization of D-RDF will not give quality defect to cement or clinker product

Keywords
Emission, Oil Sludge, Biomass, Hazardous Waste, D-RDF

Received: 27 Agustus 2019, Accepted: 26 September 2019
https://doi.org/10.26554/ijems.2019.3.3.100-105

1. INTRODUCTION

The cement production process is an intensive thermal process because it requires high temperatures in the clinkerization process so it requires a lot of fuel. The cement industry uses 20 – 40 % of the total production cost as fuel cost (Hajinezhad et al., 2016). To reduce dependence on fossil fuels, efforts have been made to substitute fuels with alternative fuels through a co-processing process with the use of waste and biomass. One of alternatives energy available and considered by PT Semen Padang is the use of oil sludge waste, which received from PT Pertamina in the range of 20 tons/month to be destroyed in a rotary kiln in the cement plant. Oil sludge is a solid waste in the form of black mud or paste, sometimes mixed with soil, gravel, water and other materials produced from the refining process, distribution process and petroleum storage tanks. Oil sludge contains hydrocarbon compounds such as benzene, toluene, ethyl benzene, xylenes, and heavy metals (Hu et al., 2013).

Utilization of oil sludge as fuel must meet emission-quality standards in accordance with the Indonesian Environment and Forestry Minister regulation 19/2017, meanwhile the trace element of D-RDF must meet the quality standards of the European Union for Responsible Incineration and Treatment of Special Waste (EURITS) for utilization of waste co-incineration in cement kilns. A large number of environmental feasibility tests have been carried out to understand the characteristics of emissions and ash by burning D-RDF as fuel in mass combustion.

To our knowledge, there has been little research on the utilization of oil sludge as an alternative fuel in cement production. In addition, there are only a few studies on the effects of various modes of adding oil sludge on clinker quality (Huang et al., 2017).

Biomass can be considered as an almost CO_2 neutral fuel (Hughes, 2000), although there are still emissions associated with harvesting, transportation, pre-treatment, etc. In addition, biomass combustion prevents the release of methane (CH_4) from residues, considering that CH_4 has a 21 times higher effect as a potential cause of global warming compared to CO2. In addition, alkaline ash from biomass can capture some CO_2 gas from burning (Saidur et al., 2011).

Most biomass fuels contain less sulfur. Therefore, co-firing with coal usually results in lower SO_2 emissions (Ren et al., 2017). NOx emissions arise from atmospheric nitrogen and from nitrogen-bound fuels, which are released during the volatilization and char oxidation phases. The release of volatile substances from biomass combustion is higher than that of coal, and during this phase, the nitrogen in the fuel is volatilized into the flame as volatile matter (Lau and Niksa, 1993). Inside the flame, nitrogen bound to biomass mostly forms NH_3 instead of HCN which is usually formed by nitrogen coal, and this can help prevent the formation of NOx in flames (Hein and Spliethoff, 1999).

Previous studies on coal combustion and rice husk jun XIE et al. (2007) reported that in the use of coal ratio remained the same and addition amount of biomass into the mixture will reduced NO emissions but slightly increased SO_2 emissions. NO reduction is associated with a lower terminal velocity of rice husk particles than coal particles, due to differences in density (Fang et al., 2004). Other research was combines coal and Municipal Solid Waste (MSW) into Circulating Fluidized Bed (CFB) (Desroches-Ducarne et al., 1998). The results showed that acid gas flue increased as the proportion of MSW increased, and, further, SOx decreased because the amount of HCl in the flue gas increased.

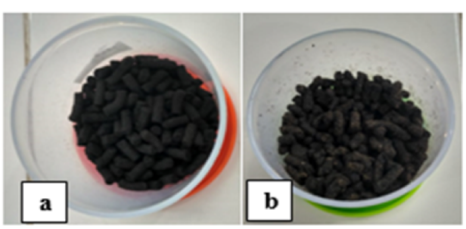

Figure 1. (a) D-RDF(A) dan (b) D-RDF(B)

In this study, D-RDF consisting of oil sludge and biomass waste is burned in the furnace to investigate the feasibility of burning D-RDF emissions. The properties of volatile matter, ash content, pollutant emissions and metal content for various fuel ratios are analyzed and discussed in this study.

2. EXPERIMENTAL SECTION

2.1 Materials

For the manufacture of D-RDF in this study, oil sludge is mixed with two types of biomass wastes, which are coconut shell powder and rice husk. The D-RDF sample can be categorized into two groups namely D-RDF (A) containing oil sludge, coconut shell powder, and 5% starch and D-RDF (B), where coconut shell powder is replaced with rice husk. For the characteristics of D-RDF raw materials can be seen in Table 1.

2.2 Equipment and Experimental

In this study, the D-RDF was produced using oil sludge as a base material and combined with coconut shell powder or rice husk with a composition of 1:1, then 5% starch is used as an adhesive to bind the raw materials. Further, raw materials are mixed in a mixer and then feed into pelletizer machine to form D-RDF. The D-RDF forms produced were cylindrical with a length of 10-16 mm, and a diameter of 5 mm. For visual form of combination of D-RDF (A) and D-RDF (B) can be seen in Figure 1.

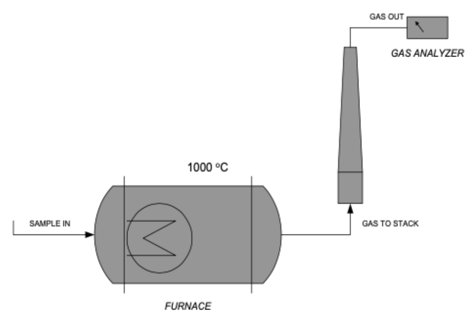

Figure 2. D-RDF Emission Measurement Scheme

To measure CO, SO2, NOx emissions from this D-RDF, it is carried out with a combustion scheme as shown in Figure 2. Probes from the Portable Gas Emissions Analyzer are inserted into the stack furnace. 1 gram D-RDF prototype was burned in the Furnace for 1 minute. The furnace temperature is set at a temperature of 1000 °C then Gas SO_2, NOx, and CO, CO_2, measured by the Gas Emission analyzer directly and the value (ppm) will be seen on the screen of the Gas emission analyzer. The D-RDF residue after combustion then analyzed for their metal content using a Shimadzu ICPE 9000TM tool. The results of the emissions analysis and metal content are compared with quality standards in the Indonesian Environment and Forestry Minister regulation 19/2017 and EURITS.

2.3 Methods

Test of calorific value of raw materials and D-RDF was carried out using the Calorimeter Bomb tool with the ASTM D 2015: Standard Test Method for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter. Moisture content, ash content, volatile matter, and fixed carbon content were measured using ASTM D3173 standard methods. Ultimate analysis using Thermo scientific CHNS / O tools with ASTM method D5373-16: Determination of Carbon,

Table 1. D-RDF Raw Material and Additive Characteristic

Parameter	Unit	Raw Material Oil Sludge	Coconut Shell	Rice Husk	Additive Starch
Proximate Analysis					
Moisture	%	34.88	10.94	10.83	13.94
Volatile Matter	%	76.13	68.08	57.44	81.39
Ash Content	%	3.14	1.55	18	0.116
Fixed Carbon	%	1.17	19.8	14.34	3.52
Calorific Value	kcal/kg	6298.86	4333.97	3381.91	3528.22
Ultimate Analysis (% dry basis)					
Carbon (C)	%	74.49	50.04	41.17	39.91
Hydrogen (H)	%	12.4	6.33	5.63	6.78
Nitrogen (N)	%	0	0.11	0.3	0
Oksigen (O)	%	8.73	41.97	35.04	50.24
Sulfur (S)	%	0.62	0.12	0.1	0.15

Table 2. Air emission limits at cement plants that implement hazardous waste co-processing based on regulation applied.

Parameter	Unit	Quality Standard
CO	mg/Nm^3	3000
SO2	mg/Nm^3	650
NOx	mg/Nm^3	800

(Source: Indonesian Environment and Forestry Minister Regulation 19/2017)

Hydrogen, and Nitrogen in Analysis of samples of Coal and Coke for measuring C, H, and N content. ASTM D 4239-17: Sulfur in the Analysis Sample of Coal and Coke is used to measure S content and ASTM D 3176-16: Ultimate Analysis of Coal and Coke is used to measure O content.

Analysis of metal content in waste oil sludge was carried out using ASTM D7260-19: Standard Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants. The oil sludge sample is dissolved first using an acid digestion method (Nitric acid), then the solution will be analyzed by ICP-AES which will measure the energy intensity of radiation emitted by the elements that experience changes in atomic energy levels (excitation or ionization).

In Indonesia, cement plants that utilize RDF co-processing and other hazardous wastes are subject to regulations issued by the Indonesian Environment and Forestry Minister regulation 19/2017 which sets CO, SO_2, and NOx emission limits as shown in Table 2.

The term trace element heavy metal has been used extensively as a term that describes the shape of certain metals. Based on research Yang et al. (2019), the characteristics of the heavy metal group are as follows:

Table 3. Physical Characteristic of D-RDF

Parameter	Unit	D-RDF Combination D-RDF(A)	D-RDF (B)
Density	g/cm^3	0,9562	0,7466
Length	mm	15	10
Diameter	mm	5	5
Drop test	%	94	77

- Has very large specific gravity (more than 4)
- Has atomic numbers 22-34 and 40-50 as well as lanthanide and actinide elements
- Has a specific (specific) biochemical response to living organisms.

Unlike ordinary metals, heavy metals usually have special effects on living things. It can be said that all heavy metals can be toxic materials that will poison the bodies of living things. Examples are mercury metal (Hg), cadmium (Cd), lead (Pb) and chromium (Cr). In general, trace elements will enter the clinker in several forms: (1) In solid solutions with various phases of calcium silicate and calcium aluminate; (2) As a substitute atom that can damage the crystal structure of these phases, such as when cobalt replaces aluminum in AFm; (3) Physically adsorbed on the surfaces of various phases as insoluble hydroxides, sulfates, or carbonates; and (4) As a precipitated mineral that is mixed with the final product, such as when molybdenum is formed forming powellite ($CaMoO_4$) at relatively high concentration of molybdenum (Horsley et al., 2016).

The quality of the final product such as clinker and cement must be controlled in accordance with applicable national or international quality standards. In principle, RDF co-processing should not reduce the quality of cement produced, where clinkers cement or concrete produced may not be used as a heavy metal dump. Apart from that, there

Table 4. Chemical Characteristic of D-RDF

Parameter	Unit	D-RDF		Lignite[c]
		D-RDF (A)[a]	D-RDF (B)[b]	
Moisture	%	9,8	11,25	-
Volatile Matter	%	73,91	69,15	49,9
Ash Content	%	2,99	12,49	11,5
Fixed Carbon	%	13,33	7,11	38,6
Calorific Value	kcal/kg	6413,17	6063,38	6
Carbon (C)	%	66,4	52,2	63,92
Hydrogen (H)	%	8,65	7,19	4,25
Oksigen (O)	%	21,56	20,38	17,71
Nitrogen (N)	%	0,03	0,01	1,51
Sulfur (S)	%	0,32	0,22	1,11

Note : D-RDF (A) = oil sludge : coconut shell (1:1) ; D-RDF (B) = oil sludge : rice husk (1:1) ; Source : (Yanik et al., 2018)

should be no negative impact on the environment.

3. RESULTS AND DISCUSSION

3.1 Physical Characteristic of D-RDF Combination

Physical characteristics of D-RDF combination; D-RDF (A) and D-RDF (B) can be seen in Table 3. Based on Table 3 it can be seen that both combination of D-RDF (A) (oil sludge: coconut shell) and D-RDF (B) (oil sludge : rice husk) have similar diameter and the length are in range 10 – 15 mm. By observing the density and drop test value it show that D-RDF (A) has better physical characteristics when compared to the D-RDF (B) because it more solid and compact.

3.2 Chemical Characteristic of D-RDF Combination

As a comparison to these D-RDF the chemical properties of lignite coal from the previous research Yanik et al. (2018) as shown in Table 4. While compared to Nitrogen and Sulfur content of Lignite, both combination shows that Nitrogen and Sulfur content are below lignite. These are mean that the source of NOx and SO2 formation from combustion are lower than what lignite potentially contributes. While compared sulfur sources (S) from oil sludge as raw material that is equal to 0.62%, Sulfur (S) values in both D-RDF variations tend to be smaller because the addition of biomass (coconut shell and rice husk) are reducing S content within the D-RDF.

3.3 Emission from Combustion

In all cement plants, whether using D-RDF or not, dust (particulate), CO, NOx, and SO_2 emissions are the main emissions that need to be addressed.

3.4 Carbon Monoxide (CO)

In this study, CO combustion values from D-RDF variations and compare with lignite combustion emission can be seen in Figure 3. In the combustion of these D-RDF variations, it can be seen that CO from the D-RDF (A) value indicates as the highest value when compared with other compositions. However, both compositions of D-RDF (A) and (B) in regards to CO emission are meeting the applicable quality standard. CO gas is formed due to lack of oxygen in the combustion process, imperfect mixing between oxygen and fuel in the combustion chamber and rapid cooling of the combustion product to lower than the ignition temperature of CO gas so that incomplete combustion occurs. CO can be formed accidentally and anywhere in the kiln system. CO gas emissions usually indicate fuel that is partially burned and not fully utilized.

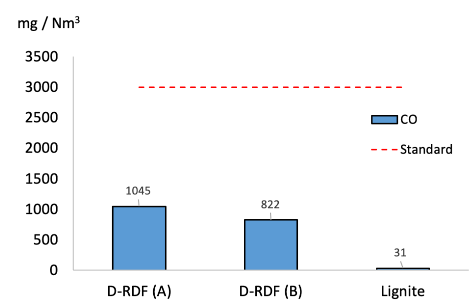

Figure 3. CO Emission of D-RDF and Lignite Figure

3.5 Sulfur Dioxide (SO_2)

SO_2 emission from D-RDF and lignite combustion could be seen in Figure 4. Sulfur dioxide (SO_2) is the result of oxidation of sulfides or sulfur elements contained in fuels during combustion and this gas is colorless with a sharp odor. The emission range depends on the content of volatile sulfur compounds in the raw material; mostly below 300 mg / Nm^3; although sometimes up to 3000 mg / Nm^3 (UNEP, 2011).

Indirect combustion, SO_2 emissions of lignite coal showed the highest value of 16,588 mg / Nm^3 when compared with other D-RDF compositions. However, based on government quality standards through the Minister of Environment and Forestry Regulation of the Republic of Indonesia, Number 19/2017, all samples both D-RDF and coal all show values above the applicable quality standard of 650 mg / Nm^3 as shown in Figure 4.

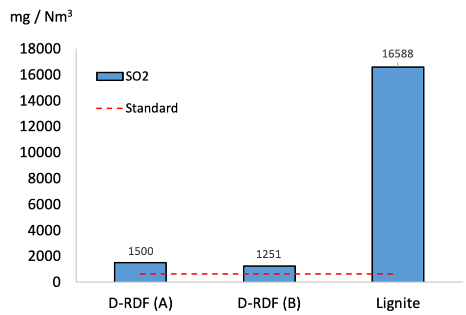

Figure 4. Comparison of SO_2 Emissions from D-RDF Composition with Lignite Coal

To reduce SO_2 content, several methods can be used including (Horkoss, 2008):

- Reduction of Sulfur content, based on the goal of a substitution strategy by reduces inputs to reduce output.
- Optimizing the clinker combustion process, conducted to reduce heat consumption, to improve clinker quality and to increase equipment life. SO_2 emission reduction is only a side effect of optimization.
- Adding $Ca(OH)_2$ to the upper stage preheater, in order as an SO_2 absorbing reagent, hydrated lime can be injected into the right location in the upper stage preheater where hydrated lime reacts with SO_2 directly.

3.6 NOx Emission

For NOx value from D-RDF and lignite combustion could be seen in Figure 5. Nitrogen Oxide (NOx) is a group of nitrogen gases found in the atmosphere consisting of Nitrogen Monoxide (NO) and Nitrogen Dioxide (NO_2). Air pollution by NOx gas can cause the emergence of Peroxy Acetyl Nitrates which is abbreviated with PAN. Peroxy Acetil Nitrates causes irritation in the eyes which causes the eyes to feel sore and runny. In combustion units, nitrogen oxides (NOx) mainly arise from three sources, namely, thermal, prompt, and fuel sources. The formation of NOx is one of the major concerns because its emission would further induce acid rain, photochemical smog, and even health hazards (Li et al., 2018).

Based on Figure 5, the standard quality of NOx value is 800 mg / Nm^3 meanwhile the results for D-RDF (A) and D-RDF (B) are still far below the applicable quality standards which are 143 mg / Nm^3 and 69 mg / Nm^3, respectively. This is due to the low content of Nitrogen (N) composition ranging from 0.01 to 0.03%. When compared to lignite coal, the NOx emission caused by lignite is higher, this is due to the lignite coal its nitrogen content is quite high at 1.51%.

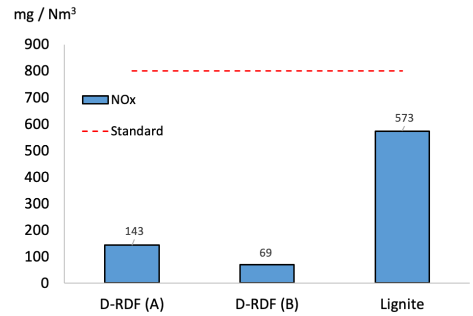

Figure 5. Comparison of NOx Emission from D-RDF Composition with Lignite Coal

3.7 Heavy Metal Content of D-RDF Ash

For the results of trace element analysis of heavy metals of D-RDF (A) and D-RDF (B) can be seen in Table 5. The results of both D-RDF for heavy metal content analysis were compared with the quality standard in fuels according to EURITS shows that there was no heavy metal in the D-RDF that exceeded the specified quality standard. Whereas in other studies Edo et al. (2017) with the composition of Demolition and Construction Wood (DC): RDF, it was found that there was an analysis of metal content that exceeded the applicable metal content, namely for As and Pb metals. This result shows that D-RDF from the of oil sludge: biomass waste combination is considerable suitable as an alternative fuel in cement industry.

4. CONCLUSIONS

In this study, an observation was made for the emissions resulting from the utilization of D-RDF mixture of oil sludge and biomass as an alternative fuel in the Cement Industry as well as the metal content of combustion residual ash. The results of this study are compared with the use of lignite coal as the main fuel for combustion in the Cement Industry. the CO content shows that both D-RDF have higher emission values than lignite, but still meet the applicable quality standards. Both of SO_2 content of D-RDF even though it is above the quality standard but is far below the result of lignite combustion, this is will make the workload of emission control devices such as ESP and Bag House Filters will be lower to reduce levels of SO_2 emissions in the utilization of D-RDF compared to lignite utilization. In the case of NOx content, both D-RDF and lignite show that NOx emission values are meet applicable emission standards. The content of the combustion ash metal shows that the D-RDF metal content meets applicable quality standards. Meaning that the utilization of D-RDF as an alternative fuel will not affect the quality of the clinker and cement produced.

Table 5. Analysis of D-RDF (A) and D-RDF (B) heavy metal content

Parameter	Unit	Standard[a]	D-RDF (A)	D-RDF (B)
As	mg/L	10	0,0238	0,0227
Cd	mg/L	10	0,0340	0,0354
Co	mg/L	200	0,126	0,131
Cr	mg/L	200	0,047	0,049
Cu	mg/L	200	0,044	0,047
Hg	mg/L	2	0,078	0,087
Mn	mg/L	200	0,052	0,055
Ni	mg/L	200	0,024	0,021
Pb	mg/L	200	0,023	0,022
Se	mg/L	10	0,021	0,02
Sn	mg/L	200	0,054	0,054
Zn	mg/L	500	0,289	0,30

REFERENCES

Desroches-Ducarne, E., E. Marty, G. Martin, and L. Delfosse' (1998). Co-combustion of coal and municipal solid waste in a circulating fluidized bed. *Fuel*, **77**(12); 1311–1315

Edo, M., N. Skoglund, Q. Gao, P.-E. Persson, and S. Jansson (2017). Fate of metals and emissions of organic pollutants from torrefaction of waste wood, MSW, and RDF. *Waste Management*, **68**; 646–652

Fang, M., L. Yang, G. Chen, Z. Shi, Z. Luo, and K. Cen (2004). Experimental study on rice husk combustion in a circulating fluidized bed. *Fuel Processing Technology*, **85**(11); 1273–1282

Hajinezhad, A., E. Z. Halimehjani, and M. Tahani (2016). Utilization of Refuse-Derived Fuel (RDF) from Urban Waste as an Alternative Fuel for Cement Factory: a Case Study. *nt. J. Renew. ENERGY Res. E.Z.Halimehjani al*, **6**(2)

Hein, K. and H. Spliethoff (1999). *Co-combustion of coal and biomass in pulverized fuel and fluidized bed systems–Activities and research in Europe*. Univ. of Stuttgart (DE)

Horkoss, S. (2008). Reducing the SO2 emission from a cement kiln. *International journal of Natural and Social Science*

Horsley, C., M. H. Emmert, and A. Sakulich (2016). Influence of alternative fuels on trace element content of ordinary portland cement. *Fuel*, **184**; 481–489

Hu, G., J. Li, and G. Zeng (2013). Recent development in the treatment of oily sludge from petroleum industry: A review. *Journal of Hazardous Materials*, **261**; 470–490

Huang, M., X. Ying, D. Shen, H. Feng, N. Li, Y. Zhou, and Y. Long (2017). Evaluation of oil sludge as an alternative fuel in the production of Portland cement clinker. *Construction and Building Materials*, **152**; 226–231

Hughes, E. (2000). Biomass cofiring: economics, policy and opportunities. *Biomass Bioenergy*, **19**; 457–465

jun XIE, J., X. min YANG, L. ZHANG, T. li DING, W. li SONG, and W. gang LIN (2007). Emissions of SO2, NO and N2O in a circulating fluidized bed combustor during co-firing coal and biomass. *Journal of Environmental Sciences*, **19**(1); 109–116

Lau, C. and S. Niksa (1993). The impact of soot on the combustion characteristics of coal particles of various types. *Combustion and Flame*, **95**(1-2); 1–21

Li, P.-W., C.-S. Chyang, and H.-W. Ni (2018). An experimental study of the effect of nitrogen origin on the formation and reduction of NOx in fluidized-bed combustion. *Energy*, **154**; 319–327

Ren, X., R. Sun, X. Meng, N. Vorobiev, M. Schiemann, and Y. A. Levendis (2017). Carbon, sulfur and nitrogen oxide emissions from combustion of pulverized raw and torrefied biomass. *Fuel*, **188**; 310–323

Saidur, R., E. Abdelaziz, A. Demirbas, M. Hossain, and S. Mekhilef (2011). A review on biomass as a fuel for boilers. *Renewable Sustainable Energy Rev*, **15**; 2262–2289

UNEP (2011). Annual Report. Technical Report 978-92-807-3244-3

Yang, J., Q. Li, J. Zhao, Y. Zhao, and J. Zhang (2019). Sorbents for trace elements in coal-derived flue gas. In *Emission and Control of Trace Elements from Coal-Derived Gas Streams*. Elsevier, pages 287–373

Yanik, J., G. Duman, O. Karlström, and A. Brink (2018). NO and SO2 emissions from combustion of raw and torrefied biomasses and their blends with lignite. *Journal of Environmental Management*, **227**; 155–161

