Article:

Gao, N, Kamran, K, Quan, C et al. (1 more author) (2020) Thermochemical conversion of sewage sludge: A critical review. Progress in Energy and Combustion Science, 79. 100843. ISSN 0360-1285

https://doi.org/10.1016/j.pecs.2020.100843

Thermochemical Conversion of Sewage Sludge: A Critical Review

Ningbo Gao[1*], Kamran Kamran[1], Cui Quan[1], Paul T. Williams[2*]

[1]School of Energy and Power Engineering, Xi'an Jiaotong University, Xi'an, China, 710049.

[2]School of Chemical & Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

*Corresponding author: *e-mail:* nbogao@xjtu.edu.cn; p.t.williams@leeds.ac.uk

Abstract: The increasing levels of sewage sludge production demands research and development to introduce more commercially feasible options for reducing socio-economic and environmental problems associated with its current treatment. Sewage sludge may be processed to produce useful products or as a feedstock for energy generation. Initially, the characteristics of sewage sludge are discussed in terms of composition and the current options for its treatment with the associated environmental impacts. Processes to valorize sewage sludge are discussed, including heavy metal removal from sewage sludge, production of bio-char, production and use of activated carbon and use of sewage sludge combustion ash in cement and concrete. Thermochemical processes i.e., pyrolysis, co-pyrolysis and catalytic pyrolysis, also gasification and combustion for process intensification, energy and resource recovery from sewage sludge are then critically reviewed in detail. The pyrolysis of sewage sludge to produce a bio-oil is covered in relation to product bio-oil composition, reactor type and the use of catalysts. Gasification of sewage sludge focusses on the characteristics of the different available reactor types and the influence of a range of process parameters and catalysts on gas yield and composition. The selection and design of catalysts are of vital importance to enhance the selectivity of the selected thermochemical pyrolysis or gasification process. The catalysts used for sewage sludge treatment need more research to enable selectivity towards the targeted desired end-products along with optimization of parametric conditions and development of innovative reactor technologies. The combustion of sewage sludge is reviewed in terms of reactor technologies, flue gas cleaning systems and pollutant emissions. In addition, reactor technologies in terms of technological strength and market competitiveness with the particular application to sewage sludge are compared for the first time for thermochemical conversion. A critical comparison is made of the drying techniques, co-feedstocks and catalytic processes, reaction kinetics, reactor technologies, operating conditions to be optimized, removal of impurities, fuel properties, their constraints and required improvements. The emphasis of this review is to promote environmental sustainability for process intensification, energy and resource recovery from pyrolysis, gasification and combustion involving the use of catalysts.

Keywords: Sewage sludge; Thermochemical; Catalysts; Pyrolysis; Gasification; Combustion.

Table of Contents

Abbreviations:

AC: Activated Carbon
AHP: Analytical Hierarchy Process
A.D: Anaerobic Digestion
BFBR: Bubbling Fluidized Bed Reactor
CCE: Carbon Conversion Efficiency
CFBR: Circulating Fluidized Bed Reactor
CGE: Cold Gas Efficiency
CHP: Combined Heat and Power
CO: Carbon Monoxide
CO_2: Carbon Dioxide
CP: Chlorinated Paraffin
CS: Cereal Straw
daf: Dry Ash Free Base
DME: Dimethyl Ether
DSC: Differential Scanning Calorimetry
DSS: Dried Sewage Sludge
DTG: Differential Thermogravimetry
ER: Equivalence Ratio
FBC: Fluidized Bed Combustor
FBR: Fluidized Bed Reactor
FTIR: Fourier Transform Infrared Spectrometry
FW: Forestry Waste
GC-MS: Gas Chromatography-Mass Spectrometer
GHG: Green House Gas
ΔH: Change in Enthalpy HCl: Hydrogen Chloride
HCN: Hydrogen Cyanide
HHV: Higher Heating Value
HM: Heavy Metal
H_2S: Hydrogen Sulfide
HTC: Hydrothermal Carbonization
LHV: Lower Heating Value
MT: Million Tonnes
MN: Manure
MSS: Municipal Sewage Sludge
N: Nitrogen
n.d: Not Detected
PCP: Personal Care Products
PFC: Perfluorinated Surfactant
PFAS: Perfluoroalkyl Substances
PFOA: Perflourooctanoate
NH_3: Ammonia
n.r: Not Reported
P: Phosphosrous
PAH: Polyaromatic Hydrocarbon
PCB: Polychlorinated Biphenyls
PCDD: Polychlorinated dibenzo-p-dioxins
PCDF: Polychlorinated dibenzofurans
PFOS: Perflouroctane Sulfonate
PhCs: Pharmaceuticals
PM: Particulate Matter
PMS: Paper Mill Sludge
PS: Paper Sludge
PW: Pinewood
PS: Primary Sludge
PSD: Pine Saw Dust
RS: Rice Straw
RSS: Raw Sewage Sludge
SBR: Spouted Bed Reactor
SCWG: Super Critical Water Gasification
SD: Saw Dust
SEM: Scanning Electron Microscope
SO_2: Sulfur Dioxide
SP: Straw Pellets
SS: Sewage Sludge
SSC: Sewage Sludge Char
S/SS: Steam to Sewage Sludge Ratio
SW: Softwood
TEM: Transmission Electron Microscope
Temp.: Temperature
TGA: Thermogravimetric Analysis
TPD: Ton Per Day
TRL: Technology Readiness Level
TS: Technological Strength
WB: Woody Biomass
WP: Wood Pellets
WS: Wheat Straw
WSS: Wet Sewage Sludge

1. Introduction

Sewage sludge is the by-product from the treatment of waste water and has the potential to be used for generating heat and power [1]. There is interest in the development of alternative routes to treat and dispose of sewage sludge driven by socio-economic and environmental concerns [2]. In addition, sewage sludge contains many organic and inorganic noxious compounds for which a sustainable treatment solution needs to be found [3]. It is estimated that about 50% of the costs for the operation of secondary sewage sludge treatment plants in Europe is directly associated with handling and disposal [4]. Sewage sludge derived from the treatment plant contains a high content of moisture, and thereby the volume and tonnages requiring treatment are large, for example, the annual wet sewage sludge production in the USA, China and Europe was estimated as 240 MT (2010) [5]. The collective generation of sewage sludge in China had a growth rate of 13% from 2007-2013, with 6.25 MT of dry solids in 2013 of which only 25% was appropriately treated. In 2017, the global sewage sludge production rate was recorded as 45 dry MT per year [1, 6-8]. In 2015, five EU countries (Germany, United Kingdom, France, Spain and Italy) were reported to produce 75% of the total sewage sludge in Europe [4]. In the same year, annual sewage sludge production in China and Taiwan was recorded as 30-40 MT and 77,000 T, respectively [8, 9]. Fig. 1 illustrates the total production of sewage sludge in different countries. The magnitude of sludge production has stimulated the search for new and alternative treatment options.

Sewage sludge poses major issues for its usage in many applications as it contains a very high moisture content at almost 98 wt.%. Generally, moisture content lower than 60% is desired before disposing through landfill, agriculture applications etc. but for thermal processing, below 15% is required [10]. Different drying operations are essentially contingent on the moisture level and operational costs before use in thermochemical processes. The different options for drying are natural drying, mechanical drying, thermal drying and bio drying [11]. Natural drying can be through for example, using solar energy to reduce moisture, while mechanical drying may not reduce the moisture content as much as thermal drying. Bio drying is similar to the composting process which may take many days to lower the moisture content. The second most important characteristic of sewage sludge is its high heavy metal content. The trace elements in sewage sludge in different regions are shown in Fig. 2. However, beneficially, sewage sludge is enriched in nitrogen and phosphorus which act as fertilizer in land applications and agriculture [12, 13].

Based upon the moisture level, contaminant level and socio-economic factors, U.S., China, Japan and EU countries have identified potential usage of sewage sludge in land applications, building materials, anaerobic digestion and incineration (Fig. 3). However, a significant amount of sewage sludge may also be disposed of by improper dumping (Fig. 3). It has been reported that the process routes for the treatment and disposal of sewage sludge in different countries are closely linked to their economic development [14].

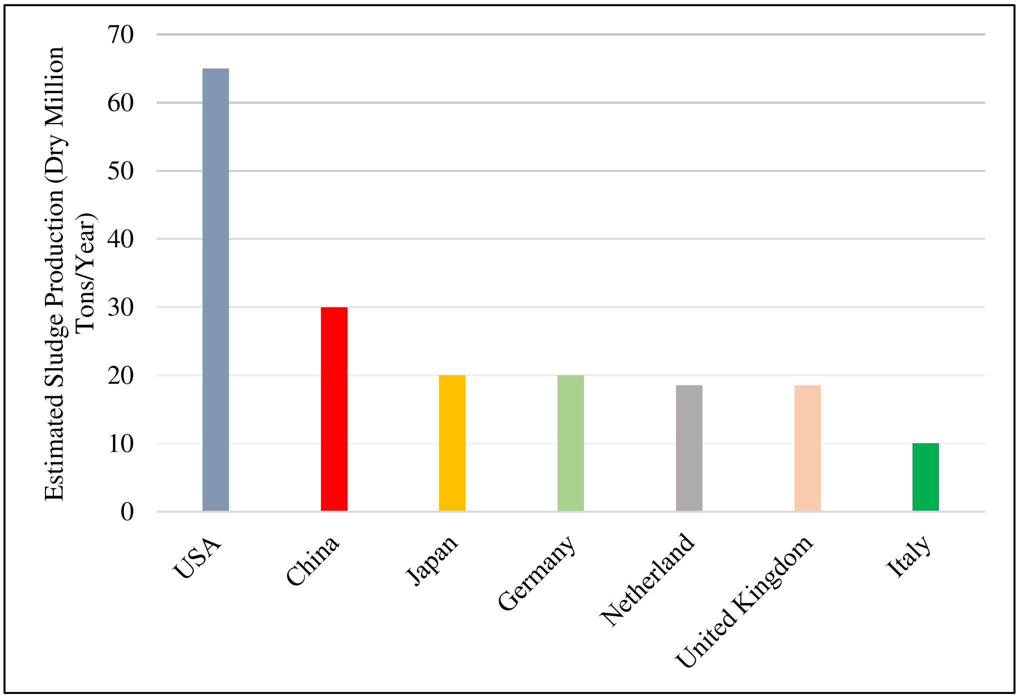


Fig. 1: Examples of estimated sewage sludge production in different countries [6, 7, 14].

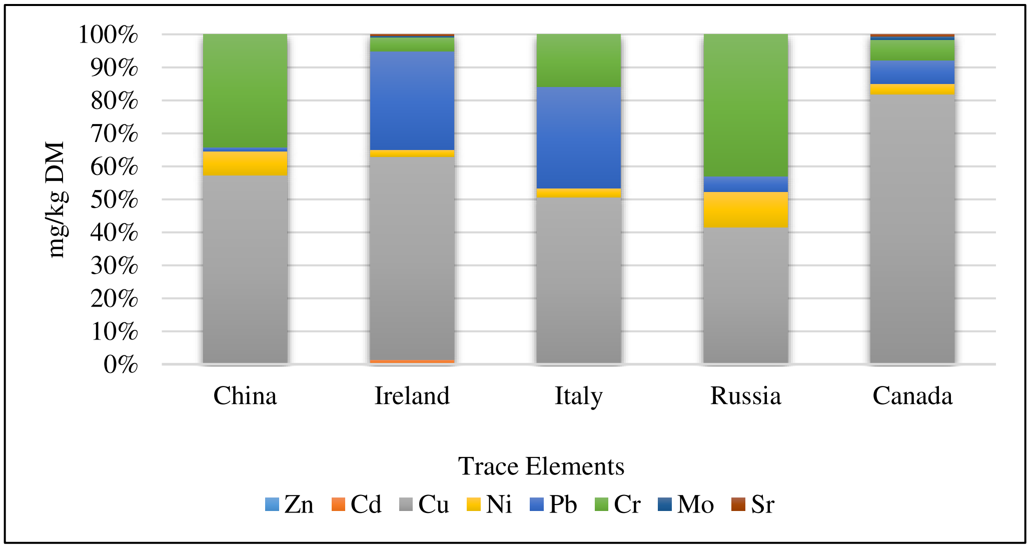


Fig. 2: Examples of the content of trace elements in sewage sludge for different countries [15-18].

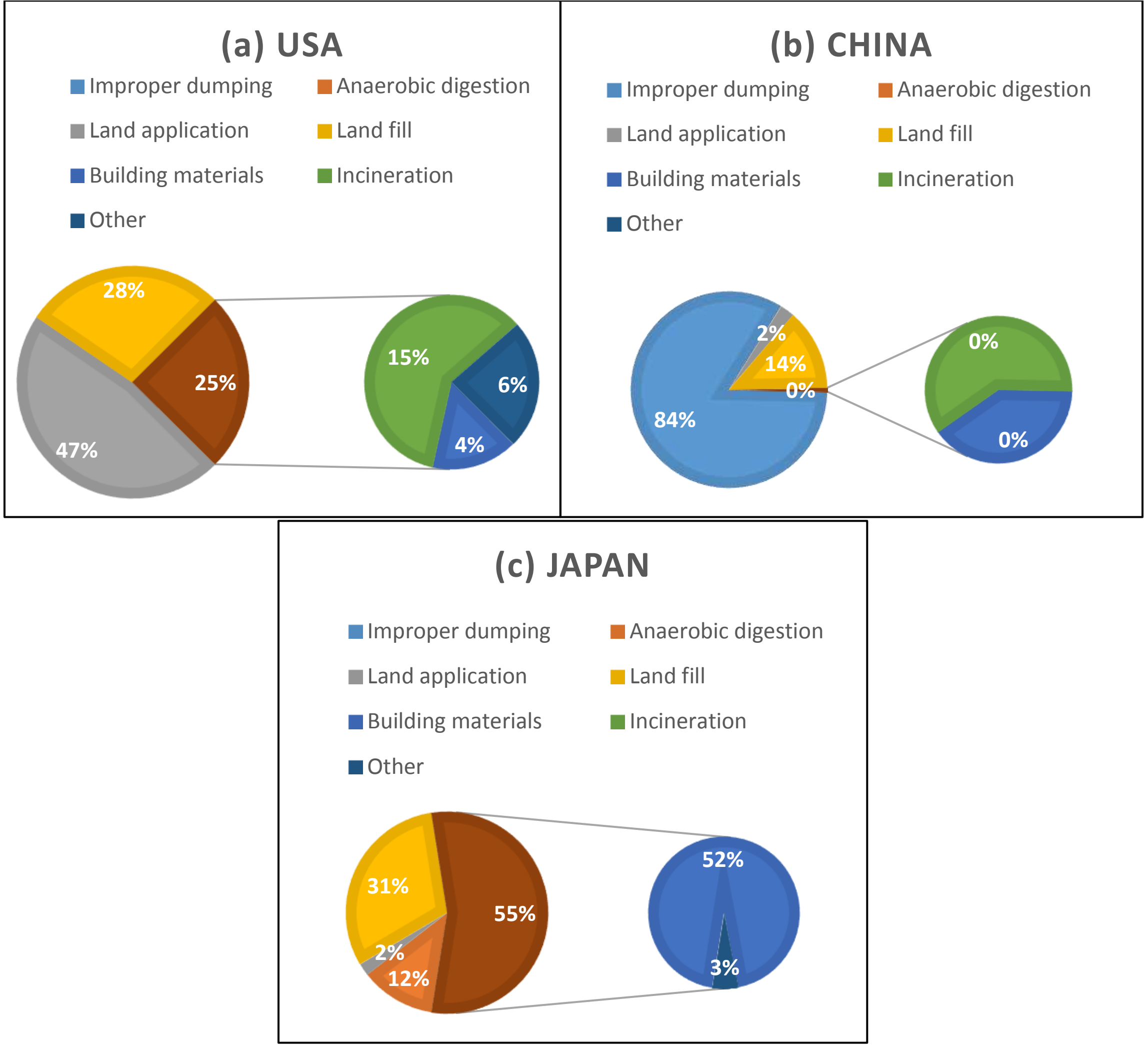


Fig. 3: Potential usage of sewage sludge in (a) USA, (b) China and (c) Japan [4, 14].

Thermochemical conversion technologies such as pyrolysis and gasification have been suggested as replacements for sewage sludge energy recovery rather than the current most used options [19]. Each thermochemical process has its own technological and socio-economic merits and demerits which are discussed in Sections 4 to 6 of this manuscript. Although thermo-chemical conversion involves complex equipment or processes, compared to other treatment processes, they may exhibit better economic performance, higher efficiency and greater volume reduction. A recent detailed comparison of the merits and de-merits of different processes, operational costs and operating conditions of microbiological methods and thermochemical methods has been made [18]. It was concluded that anaerobic digestion requires a solids retention time of several days, a large space requirement for the digesters, low variety of products and supplementary capital investment compared with thermochemical processes [18]. There is current interest in sewage sludge management in relation to the topics of process intensification, sludge contaminants, resource recovery, innovative treatment processes and costs [20]. In several thermochemical treatment processes, many researchers have investigated the use of a variety of catalysts to intensify the process and to produce end-products having higher value.

Pyrolysis is advantageous for the decomposition of organic pollutants, neutralization of pathogens, and reduction of the volume of the waste. The resultant products derived from sewage sludge pyrolysis are light gases containing H_2, CO, CO_2 and CH_4, bio-oil, and char. [21]. The generation of bio-oil and char is reliant on moisture content and ash content of the feedstock, operating conditions, catalyst and the reactor type to be used. Gasification is a thermochemical process for the production of syngas and also as a promising route for H_2 production. The main product from gasification is syngas comprising of CO and H_2, but may also contain, CH_4, H_2O and also tar as a by-product. The tar that evolves during the gasification process results in many problems for the end-use of the product gas such as blockage of down-stream pipelines, valves and fuel injector nozzles, that are needed to be solved to allow viable development of the gasification process [22]. Similarly, direct combustion and co-combustion of sewage sludge is also developing in many countries which is associated with a negative environmental impact compared with pyrolysis and gasification. Recently, researchers have also worked on processing of the wet sewage sludge directly through hydrothermal treatment, supercritical water gasification (SCWG) and the use of plasma reactors. For dewatering and generating energy from sewage sludge, hydrothermal treatment has been reported to be efficient [23]. Hydrothermal treatment consists of carbonization and liquefaction at elevated pressure in which water acts both as a reactant and a solvent [24]. The costs involved for hydrothermal treatment tend to be higher than pyrolysis due to the higher pressures involved. Fig. 4 represents an overview of sludge production and thermochemical processes which can be used for energy recovery.

There have been several reviews on the pyrolysis of sewage sludge, for example, Fonts et al. [25] have presented a detailed review on pyrolysis of sewage sludge for liquid production, Hassan et al. [26] and Manara et al. [27] have also presented overviews of the thermochemical conversion of sewage sludge. They have discussed non-catalytic pyrolysis, gasification and combustion of sewage sludge. Therefore, to advance the field of research a comprehensive and critical review on the catalytic thermochemical conversion with respect to the characteristics of sewage sludge is required. Thermochemical processes for the treatment of sewage sludge can be enhanced by the use of catalysts in terms of selectivity of the higher value end-product and process efficiencies, ensuring the most suitable catalyst is used and with an appropriate reactor system. In this review, the influence of the different characteristics of sewage sludge on the catalytic process, the range of catalysts used and their effects on product yield and composition and process efficiency are discussed. In addition, the important factors of technological strength and market competitiveness of reactor technologies are presented.

Therefore, the domain of this paper includes; drying processes to reduce the moisture of sewage sludge, regulations in different countries regarding pollutants and heavy metals, and catalytic thermochemical processes for energy recovery. A comprehensive comparison of pyrolysis, co-pyrolysis and catalytic pyrolysis and gasification, co-gasification and catalytic gasification is presented in order to identify issues for such enhanced processes, energy and resource recovery. Utilization of char and ash derived from sewage sludge is discussed in applications such as adsorbents, catalysts, building materials and agriculture. An emphasis is placed on reviewing the role of catalysts and combinations of different catalysts with their promotors, supports, catalytic activity, selectivity, coke deposition and deactivation problems related to the produced end-products by considering the influence of sewage sludge properties such as high ash content on product yield and composition. A comparison of the previous research and reported conclusions have been reviewed in regard to modern technological advancements, which are necessary to identify challenges and limitations towards their development for processing sewage sludge.

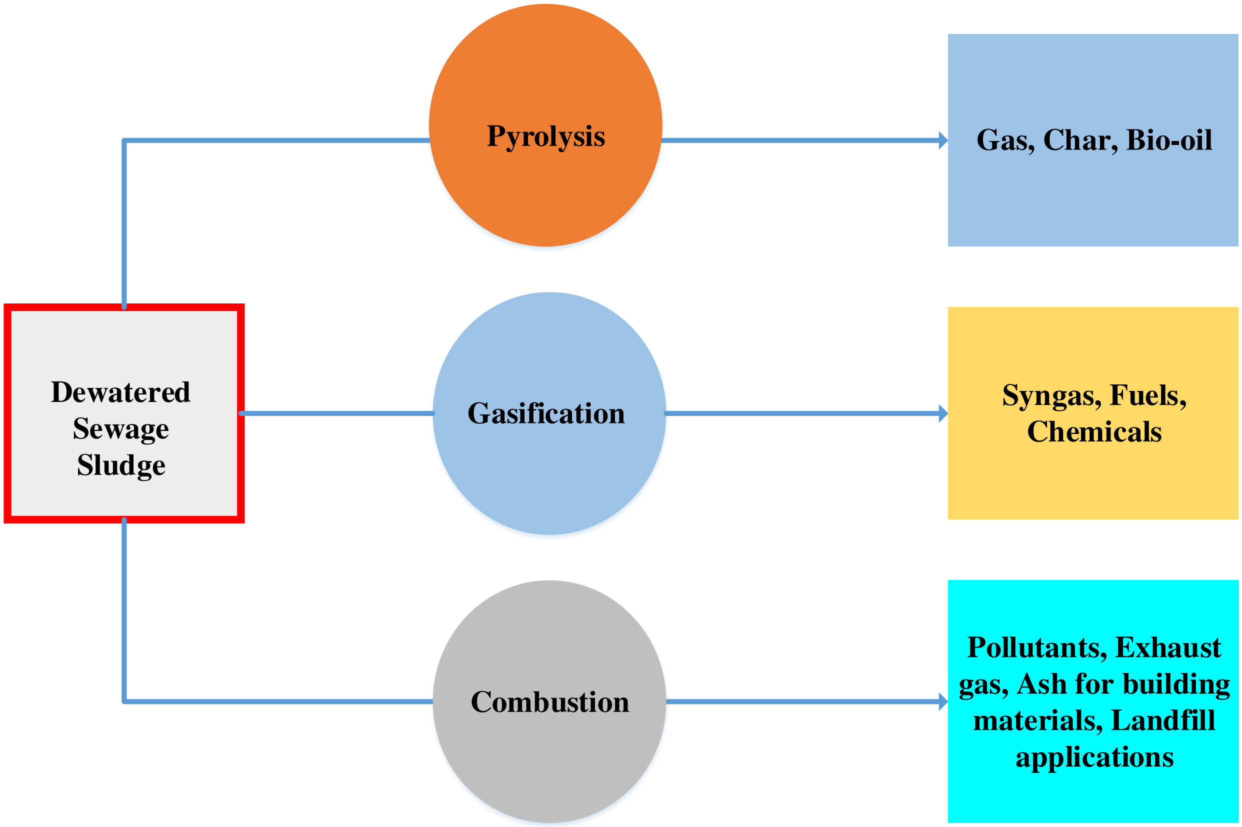


Fig. 4: Schematic diagram of thermochemical processes for sewage sludge.

2. Characteristics of Sewage Sludge

2.1 High Moisture Content

There are different categories of sewage sludge which includes primary, waste activated and digested sludge that can be converted into useful energy [28]. In water treatment plants, the purified water is separated out leaving the sewage sludge which resembles a slurry containing a significant content of water. Before using the sewage sludge, either for disposal or recovering energy, this moisture content has to be reduced to minimum levels using several available drying technique options. There are different types of drying methods for solid waste which includes sewage sludge. These drying methods include bio drying, thermal drying (fry drying and traditional air drying), and mechanical dewatering. Thermal dryers are tray, pneumatic, rotary, tunnel and cyclone dryers. While for mechanical dewatering, filter presses such as belt and vacuum methods are common [11, 29]. In terms of co-processing, many other feed stocks such as straws, wastes from cotton and wood or pre-dried feed stocks are also commonly added as bulking agents for drying of sewage sludge. Bio drying is also being used for sewage sludge in which bacteria and fungi are involved for water removal. The important parameters are initial moisture content, flow rate of air, total time of process and temperature. Nevertheless, there are drawbacks in such processes as it may take several days for drying, and the degree of moisture removal is lower compared to thermal drying [30, 31]. Pressurized electro-osmotic dewatering coupled with bio drying can reduce moisture content from 83% to 60% in a matter of minutes under optimal processing conditions [32]. A dewatering process involving propane hydrate formation for drying of sewage sludge has been reported and shown to require less energy than mechanical or thermal drying processes and can reduce moisture content by up to ~43%, however this may take several hours of operation [33]. Pathogens in sewage sludge can be reduced using drying processes based on drum drying, agitated conductive drying, solar drying, and fry-drying [34]. Drying through the use of natural solar energy is effective for drying sewage sludge but can involve several days of exposure and is dependent on weather conditions. Also, closed solar drying has been shown to be more efficient than open solar drying [35]. If the purpose of using sewage sludge is to produce energy and fuels, thermal drying is the optimal method [11]. It is evident that thermal drying is useful for not only reducing harmful bacteria and other toxic contaminants but is also effective in terms of a higher drying rate. During continuous thermal drying, nitrogen might be released at temperatures under 160-200°C, this nitrogen can be recovered for production of fertilizer [36]. The important factor to consider is the cost of the drying operation for water removal efficiency through mass and energy balances which can indicate the viability of the drying process. Before using sewage sludge in thermochemical processes, conditioners or additives such as CaO are also commonly used and are effective for drying and conditioning. A comparison of various different drying techniques is given in Table 1.

Table 1: Drying techniques for sewage sludge.

Drying Technique	Details	Results	Ref.
Bio drying	Effect of air flow rate was studied with initial water content of 59%, 68 % and 78%.	Initial moisture content has more effect rather than air flow rate.	[30]
Pressurized electro osmotic Dewatering with Bio drying	Sewage sludge sample was used with and without inoculant.	Moisture content was reduced to 60% from 84% within 7.5min and 0.0657kWh.	[32]

Free Conditioning Dewatering	The efficiency of water conversion to hydrates was calculated in 14 batches.	Energy consumption of hydrate based dewatering was almost half 2673.5kWh/t dry solid of thermal drying process.	[33]
Thermal drying	Kinetic reduction of pathogens in different drying processes.	Hepatitis-A virus can survive by solar drying but substantial reduction results have been seen by drum and fry drying.	[34]
Thermal drying	Used electromagnetic induction (200-300V) with addition of CaO and Saw dust.	Moisture content was reduced to 7% from 84% during 30 min.	[37]
Bio drying	Sewage sludge, bio drying product and saw dust were mixed at 3:2:1 ratio.	Moisture content was decreased from 66.1% to 54.7% in 20 days.	[38]

2.2 Heavy Metal and Organic Pollutant Content

The presence of heavy metals and other hazardous organic pollutant compounds in sewage sludge are key challenges for their utilization. Municipal and industrial wastewater is treated to eradicate the toxins produced by municipal and industrial accumulation [39] but sewage sludge remains contaminated by a wide range of organic micro pollutants [40]. Sewage sludge is a multifarious amalgam of microorganisms, undigested organic material like paper, plant residues, oils, or fecal material, in-organic constituents and water. There is serious concern as to the impact on human health and the environment arising from the hazardous constituents found in sewage sludge i.e., CPs [41], PAHs, PCB, PFCs, PCPs, PhCs, benzotriazoles, PFAS, nanoparticles, pesticides and surfactants [15, 42-51]. PFAS arise from many industrial processes which include metal plating, paints and coatings, fire-fighting foams, textile and leather production. PFAS mainly consist of PFOA and PFOS [52-57]. PFAS are a serious hazard to human health and ecological life. The traces of PFAS can also be found in the char derived from the pyrolysis of sewage sludge. Many countries have also introduced regulations to control these deleterious compounds. The undigested organic constituents consist of an exceedingly complex mixture of fragments obtained from proteins, peptides, lipids, polysaccharides, plant macromolecules with phenolic structures or aliphatic structures along with organic toxins [58, 59]. In the U.S., alkyl-phenol ethoxylates are extensively used as surfactants in commercial and industrial products, which have toxic effects when used in land application [60]. Most of the literature related to the impact of sewage sludge on the environment is focused on a selected number of compounds or family of compounds. Some researchers have comprehensively reviewed the key extraction techniques, cleaning procedures and instrumental techniques used for the identification of emerging toxins [61, 62]. Thus, before deploying sewage sludge to landfill or in agriculture, a detailed analysis of such emerging contaminants contained in the sewage sludge needs to be carried out. However, few countries have very strict regulations with described limit values for these pollutants. Table 2 represents the characteristics of raw sludge from waste water treatment plants and shows that concentrations of different pollutants varies from primary to secondary sludge and contains nitrogen, phosphorous, proteins, fats, organic acids, silica and iron. The contaminants of nitrogen and phosphorous can be recovered from sewage sludge through chemical and biological treatment and used as nutrients in agricultural applications.

It has been shown that there is significant energy content in the sewage sludge solids with the reported heating values of raw sludge and activated sludge at 23-29 MJ/kg and 16-23 MJ/kg respectively [63]. These statistics of primary and secondary sewage sludge suggests that, products with sufficient energy can be generated. Table 3 illustrates the proximate and ultimate analyses of sewage sludge, which shows that sewage sludge has a considerable amount of volatile matter and carbon content. However, high ash content can create problems for product and process efficiency. The oxygen content is typically between 19-31 wt.% which can affect the quality of the products, especially, during bio-oil production from sewage sludge where high oxygen and ash content may deteriorate its heating value.

Sewage sludge contains significant quantities of heavy metals, for example, zinc, copper, chromium, nickel, lead and cadmium [15]. Heavy metal chemical species distribution can be changed during the sewage treatment process of conditioning and may lead to immobilization of some heavy metals such as Pb [64]. To mitigate the effects of heavy metals in sewage sludge, the addition of lignocellulosic biomass is commonly used to produce bio fuels and bio materials [65]. Sewage sludge combustion at low temperature has been shown to transform the heavy metals like Cd, Cr, Cu, Pb, and Zn to a stable form and could decrease the leaching of heavy metals, for example, leaching of Cr and Cu have been decreased by 97.56% and 98.52% [66, 67]. Table 4 shows the limit values of different heavy metals in Europe to restrict their associated hazard in soil and land applications. Many studies based upon eco toxicological evaluations have been performed which suggest that its application to land may lead to deterioration in soil quality and reduced plant growth [68]. However, the char produced during pyrolysis of sewage sludge has been shown to have positive results in regard to copper adsorption [69]. Moreover, due to the wide variety of industrial processes feeding into the wastewater treatment plant, sewage sludge may contain significant concentrations of toxic heavy metals and organic micro-pollutants. The most toxic metals are Hg, Cd, Cu, Zn, Se, Ni, As and Cr. In Table 5, concentrations of PAHs, PhCs, PFAS are shown, which suggests that disposal of raw sewage sludge to landfill or agricultural land is not sustainable and has the potential to create many health problems. Hence, risk assessments are required before the use of sewage sludge in agriculture or land applications via chemical and biological scrutiny. Based upon these risk assessments and results obtained, sets of regulations have been developed in advanced countries.

Table 2: Characteristics of primary and secondary sewage sludge.

Parameter	PS [70]	S.S[70]	PS [71]	S.S[71]	PS[72]	S.S[72]	S.S[73]
Total dry solids (wt.%)	5-9	0.8-1.2	27.58	25.36	27.58	25.36	0.83-12
Volatile solids (wt.%)	60-80	59-68	60-80	59-68	18.8	15.5	30.88
Nitrogen (wt.%)	1.5-4	2.4-5.0	33.82	49.91	33.82	49.91	1.5-6
Phosphorous (wt.%)	0.8-2.8	0.5-0.71	n. r	n. r	34.13	28.76	0.8-11
Potash (wt.%)	0-1	0.5-0.71	n. r	n. r	n. r	n. r	0.4-3
Cellulose (wt.%)	8-15	7-9.7	n. r	n. r	n. r	n. r	n. r
Iron (Fe g/kg)	2-4	n. r	n. r	n. r	n. r	n. r	n. r
Silica (wt.%)	15-20	n. r	n. r	n. r	n. r	n. r	10-20
pH	5-8	6.5-8	n. r	n. r	5.61	6.42	5-8
Fats (wt.%)	7-35	5-12		n. r	n. r	n. r	n. r
Protein (wt.%)	20-30	33-41	2-30	32-41	n. r	n. r	15-41
Alkalinity (mg/L as $CaCO_3$)	500-1500	580-1100	n. r	n. r	n. r	n. r	n. r
Organic acids (mg/L as acetate)	200-2000	1100-1700	n. r	n. r	n. r		200-2000
Energy content (kJ/kg TS)	23,000-29,000	19,000-23,000	23000-29000	19000-23000	n. r	n. r	n. r

wt.%= weight as per dry basis, PS= primary sludge, SS= secondary sludge, n. r= not reported.

Table 3: Proximate and ultimate analyses of sewage sludge.

Proximate Analysis (wt.%)	[74]	[75]	[76]	[77]	[78]	[79]	[80]
Moisture Content	6.1^b	7.65^b	7.33^b	10.84^b	1.05^b	78^a	2.37^b
Volatiles Matter Content	53.0^b	51.66^b	62.97^b	48.31^b	47.92^b	55.8^c	45.47^b
Ash Content	38.4^b	35.02^b	16.33^b	33.88^b	45.51^b	33.7^c	45.81^b
Fixed Carbon	8.6^b	5.67^e	13.37^e	6.97^e	5.52^e	10.5^c	6.35^e
Higher Heating Value (HHV) MJ/kg	13.9	13.16	15.2	11.79	-	-	11.14
Ultimate Analysis (wt. %)							
C	31.1^b	58.5^d	38.28^a	27.38^a	25.93^b	32.8^b	24.63^b
H	4.2^b	5.8^d	5.92^a	3.92^a	4.21^b	10.2^b	3.32^b
N	3.3^b	0.53^d	1.00^a	9.90^a	4.78^b	5.4^b	2.96^b
S	1.1^b	1.43^d	0.09^a	0.45^a	1.03^b	1.7^b	1.06^b
O	24.3^b	33.74^e	31.06^e	13.64^e	22.02^b	24.5^b	19.85^e

a= as received, b= dry basis, c= moisture free basis, d= dry ash free basis, e= by difference.

Table 4: Heavy metals present in sewage sludge and their allowable limits in E.U.

Elements	Concentration (mg/kg DM)	Allowable Range (mg/kg DM)	Ref.
As	5.6-56.1	n. l	[15, 81]
Ba	41.5-1300	n. l	[15, 81]
Cd	0.83 ± 0.06	20-40	[15, 81, 82]
Cr	18.6± 2.2	n. l	[15, 81, 82]
Pb	4.0-429.8	750-1200	[18, 81]
Hg	0.1-1.1	16-25	[81]

Mo	1.7-75	n. l	[18, 81]
Ni	8.6-420	300-400	[18, 81]
Se	2	n. l	[18, 81]
Zn	0.0-7500	2500-4000	[81]
Cu	75.8± 7.0	1000-1750	[81, 82]

DM= Dry matter, n. l= no limit.

Table 5: Concentrations of PAHs, PhCs and PFAS present in sewage sludge in different countries of E.U.

Compounds	**Concentration (ng/g)**	**Ref.**
PAHs		
Benzo pyrene	17.9-1475.5	[15]
Anthracene	13-724	[15, 83]
Phenanthrene	13-5552.2	[15, 83]
Pyrene	47.2-26337	[15, 83]
Chrysene	21-2020.5	[15, 83]
Fluoranthene	34.5-3216.8	[15, 83]
Benzo Flouranthene	9.9-1477	[15, 83]
PhCs found in sewage sludge amended soils		
Diclofenace	1.16	[84-86]
Ibuprofen	5.03	[84-86]
Triclosan	833	[84, 85]
Galaxolide	633	[84, 85]
Trimethoprim	0.64	[84, 85]
Caffeine	n. d	[84, 85]
Ciprofloxacin	350-400	[84, 85]
Tonalide	113	[84, 85]
PFAS		
PFOA	1.22	[53]
PFOS	1.31	[53]
PFOA	1	[87]
PFOS	5	[87]

n. d= not detected.

3. Thermochemical Routes to Recover Energy from Sewage Sludge

Sewage sludge is known to contain a significant recoverable energy content but with the disadvantages of having high moisture, ash, heavy metals and organic pollutant contents. The routes to energy recovery involve biological and chemical options. The biological means to recover energy from sewage sludge include anaerobic digestion (AD) which has advantages in financial terms, but may produce an adverse effect on the environment via emission of pollutants [88]. Therefore, selecting the most suitable method for energy recovery should involve consideration of the various technologies, involving environmental and economic benefits in terms of resource and energy recovery [89, 90]. It has been reported that the Technology Readiness Level (TRL) for the treatment of sewage sludge is TRL 6-7 for gasification, TRL 5 for pyrolysis and TRL 6 for hydrothermal treatment, in terms of commercial viability [20]. Sewage sludge needs proper treatment which can not only mitigate the contaminants and pollutants but also recover resource and energy. In this regard, thermochemical treatment via pyrolysis, gasification and combustion have the potential in the longer term to be viable considering the cost, quality and wide range of products that can be produced and the potential of resource recovery. Energy recovery from sewage sludge has benefits for improvement of environmental impacts by resource diminution [91]. However, most of the thermochemical processes especially including the use of catalysts are still under development for the production of energy from sewage sludge. Some processes are at the demonstration phase but few have been implemented successfully. Thermochemical treatment is attractive in terms of sludge volume reduction, destruction of harmful bacteria, production of a wide range of products and importantly significant energy recovery. Use of catalysts and additives to enhance the quality and quantity of products from thermochemical processes is gaining interest and importance.

4. Pyrolysis of Sewage Sludge

4.1 Non-Catalytic Pyrolysis

Pyrolysis is deemed as a favorable sludge treatment option because it transforms sewage sludge to produce bio-oil, bio-char and gas (H_2, CO and other light gases) with minimum emission of pollutants at a low to medium operational temperature range in an inert atmosphere. Specifically, pyrolysis involves the thermal decomposition of the sewage sludge solids at temperatures ranging from 400-600°C in a non-oxygen atmosphere (using N_2 and CO_2 as inert gas) to produce the desired targeted products [25, 92]. The different types of pyrolysis technologies include slow pyrolysis, fast pyrolysis, vacuum pyrolysis, flash pyrolysis and hydro pyrolysis. The key important parameters that influence the pyrolysis process are, reactant residence time, temperature, heating rate and feedstock size. Pyrolysis has been used to process a large variety of feed stocks including, plastics, municipal solid waste, sewage sludge, oily sludge and woody biomass.

4.1.1 Torrefaction and HTC

Slow pyrolysis has low heating rates and longer residence time, and is characterized as carbonization or torrefaction. Generally, carbonization or torrefaction involves low temperatures of less than 400°C to reduce the moisture content and increase the density and grindability of the torrified char. Slow pyrolysis or carbonization results in more char with a lower quantity of bio-oil and gas. This solid residue is also called charcoal. The torrefaction process not only reduces the mass of sewage sludge but also removes the NOx, SOx and other pollutants and improves the heating value and C/H ratio of sewage sludge [93, 94]. The solid torrefied sewage sludge upon combustion at 900°C gives significant reduction in NH_3 (46%) [95]. Also, torrefied sewage sludge or biomass can also be used with each other to produce a mainly bio-char product. Important factors to consider are mass and energy balances to determine the efficiency of torrefaction of sewage sludge. Studies have shown that the HHV of the torrified char increased up to a temperature of 270°C and above that decreased in terms of energy and mass yields as the process temperature was increased [96]. Moreover, volatile content of the char decreased slowly with an increase in ash content as shown in Fig. 5 (a) and 5(b). When this residue is used in pyrolysis, co-pyrolysis or gasification processes the energy content of the product oil may increase with lowered oxygen and higher heating value. For example, a three stage process can be used, first torrefaction, followed by pyrolysis and then gasification to produce high quality bio-oil, char and gas [97].

Another thermochemical process to produce bio-char is hydrothermal carbonization (HTC). The solid residue left is also called hydro char. This treatment is beneficial for wet sewage sludge having 70-80% moisture content to produce hydro char, liquid and a nominal amount of CO_2 under the temperature range of 180-250°C in a closed vessel under pressure [23, 24, 98-102]. For wet sewage sludge, microwave pyrolysis is also common but reported to be not effective [103]. If the moisture content in sewage sludge is not removed properly, then during the thermochemical process most of the energy would be used in removing water. The specific heating value of char obtained by hydrothermal carbonization may be less than pyrolysis char. HTC is an interesting option for prior treatment before pyrolysis because it reduces the heavy metal content [104]. Thus, torrefaction and hydrothermal carbonization methods are favorable to produce stabilized bio-char for further use in pyrolysis, gasification or combustion.

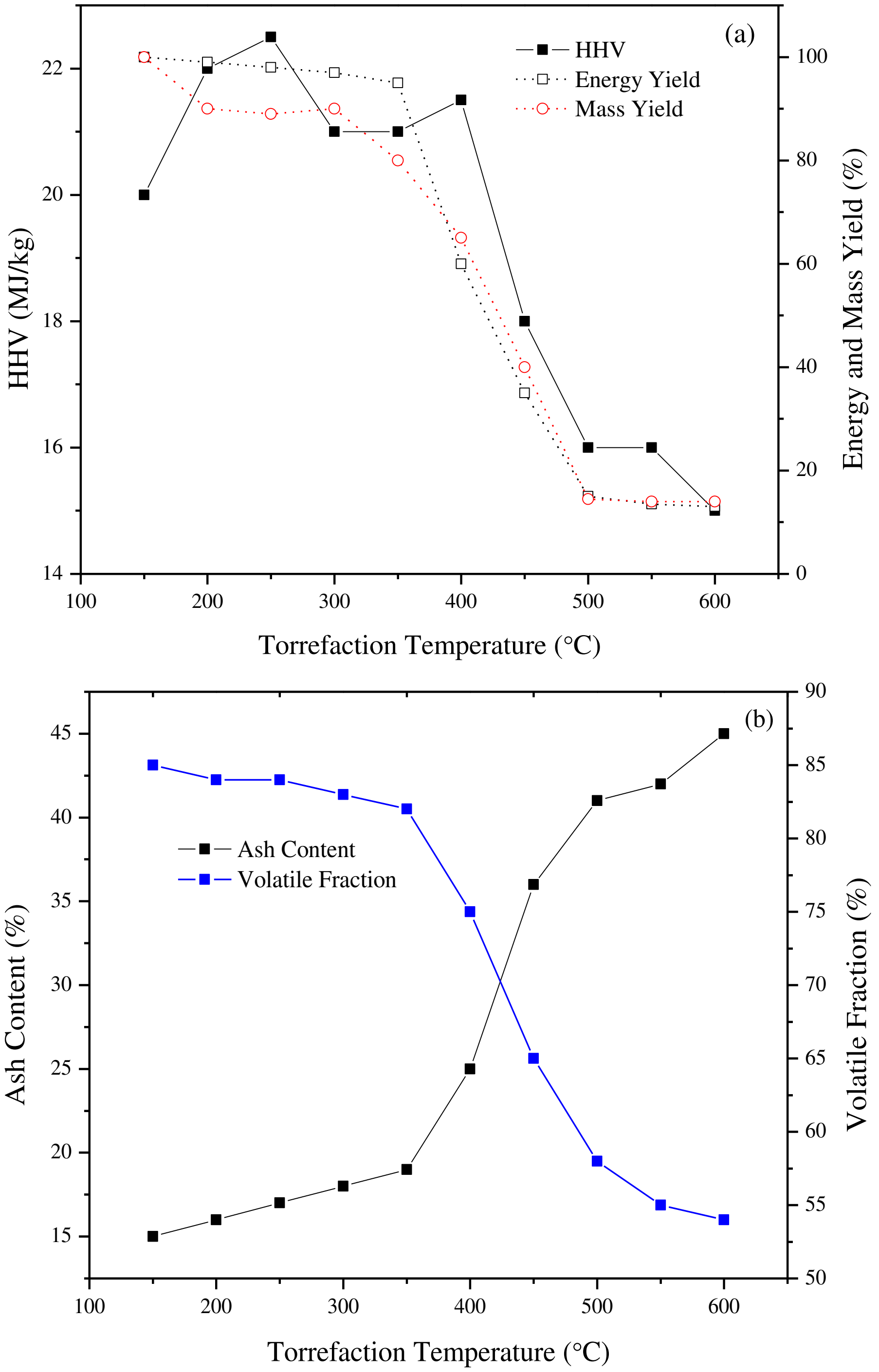


Fig. 5: Effect of torrefaction temperature on (a) HHV, energy yield and mass yield [94-96] (b) ash content and volatile fraction [96]. (Trend for HHV at 220°C: 25MJ/kg, 270°C: 28 MJ/kg and 320°C: 25 MJ/kg is found in [93] [94] and [95], while [96] studied up-to 600°C and gave a clear idea for HHV, mass and energy yields, ash and volatile matter).

4.1.2 Fast Pyrolysis

The fast pyrolysis process has been used for the conversion of sewage sludge to a bio-oil product.

The operational conditions for fast pyrolysis are different from slow pyrolysis, the main difference is higher heating rate and short residence time with a temperature range of 400-600°C. Fig. 6 shows that more yield of bio-oil is obtained at a pyrolysis temperature of around 570°C. The product distribution from fast pyrolysis shows a higher yield of bio-oil rather than char and gas.

(a) Bio-oil Properties

Fast pyrolysis has been studied by several researchers with the aim of producing bio-oil. Bio-oil produced from pyrolysis of sewage sludge consists of hydrocarbons, organic acids and carbonyl compounds of high molecular weight, phenols, ketones, aromatic and aliphatic compounds, alcohols, acetic acid, nitrogenous compounds, sulfur compounds and water as shown in Table 6 [27, 75, 105-107]. Table 7 presents the characteristics of sewage sludge pyrolytic oil in comparison with petroleum derived heavy fuel oil. The bio-oil has more moisture than heavy fuel oil due to the presence of oxygenated compounds which lead to two phases, light and rich organic oil. The light organic phase has mainly water and the heavy phase is rich in benzene, toluene, styrene, naphthalene and phenol etc. [108]. The average HHV is around 30 MJ/kg which is less than the HHV of petroleum fuel oil 40 MJ/kg. The presence of initial water content and decomposition of volatile matter during the pyrolysis results in low heating value and oxygenated compounds in the product bio-oil. The commercial use of this bio-oil is in heating and combustion, however its low HHV is a constraint in this process. The properties of bio-oil can be enhanced by using co-pyrolysis and by use of suitable catalysts. To increase the C/H ratio and to decrease the oxygen level in the bio-oil many studies have been carried out with variation in results.

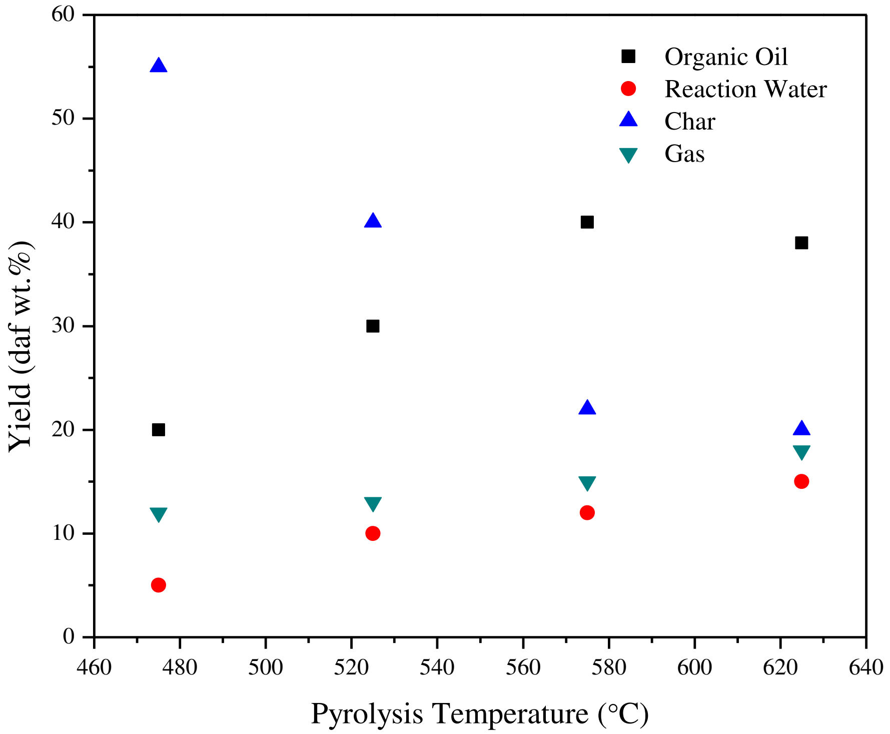


Fig. 6: Yield (daf wt.%) of bio-oil, char and gas with respect to temperature [105, 109, 110]. (Bio-oil yields in [105, 109, 110] are almost 40% at around 575°C, however due to different operating conditions char and gas yields are varied. To have more clear picture readers can see the references).

Table 6: Chemical families present in sewage sludge pyrolytic bio-oil from 450-700°C [107, 111-113].

Compounds	Concentration (wt.%)
Oxygenated Compounds	
Acids	2.07-5.53
Ketones	2.82-11.72
Phenols	15.28-18.03
Alcohols	4.65-6.36
Furans	2.34-3.10
Ethers	0.84-1.87
Esters	0.58-0.88
Sacchrides	2.23-4.44
Aldehydes	0.45-1.74
Carboxylic anhydrides	0.09-0.31
Hydrocarbons	
Aromatic	0.33-9.21
Aliphatic	0.27-0.29
Nitrogen containing compounds	
Nitriles	1.49-2.73
Pyridines	0.42-0.57
Pyrazines	1.07-1.51
Amines	1.06-1.47
Amides	1.27-1.45
Pyrroles	2.48-4.78
Sulfur Compounds	0.98-1.23

Table 7: Properties of bio-oil in comparison with heavy fuel oil.

Property	SS bio-oil					Heavy fuel oil
	[114]	[97]	[39]	[111]	[112]	[26, 111, 115]^d
Water Content (wt.%)	46.6	-	13.3	23	10.9	0.1
pH	-	-	9.3	8.5	6.8	-
Density (kg/m^3)	975	-	1026	1050	1100	940
Viscosity (cSt)	16.91	-	52	28		180
Elemental Composition (wt.%)						
C	-	74.5^c	65.2^a	45^a	65.2^a	85
H	-	8.8^c	7.6^a	8.8^a	8.6^a	11
N	-	10.1c	7.6^a	6.6^a	8.4^a	0.3
S	-	1.3^c	1.2^a	0.7^a	0.4^a	0.28
O	-	5.3^c	4.5^a	39^a	17.4^b	1
HHV (MJ/kg)	31.87	31.1	30.2	18.8	36.4	40

a= as received, b=by difference, c= moisture free basis, d= reported heavy fuel properties.

(b) Bio-char as an Adsorbent

The char obtained from the fast pyrolysis process contains carbonaceous material and has been used as adsorbent due to having high surface area or as further use in gasification processes to produce syngas and chemicals. The heating value of the chars depends mainly on the feedstock and the values may vary from 11-15 MJ/kg. However, pH, ash, specific surface area and heavy metal content may increase at higher pyrolysis temperatures and heating rates [116-118]. Sewage sludge has been investigated for the production of char by the pyrolysis process or physical and chemical activation of sewage sludge to produce activated carbons. The activated carbons may have a high surface area and low ash content. The surface area can be increased by KOH activation to produce activated carbons of surface area up to 1800 m^2/g. As the major part of the sewage sludge is composed of carbonaceous materials containing different metals, the produced char from the pyrolysis process with modification may be used as an adsorbent for pollutants. It has been seen that during waste water treatment the dispersed particles settle by gravity and the use of agglomerates or coagulants which are mostly salts of iron and aluminum. The aluminum and iron hydroxides of sewage sludge have an amorphous nature which makes an adsorption site for anions. More iron content in sewage sludge is useful for waste water treatment from vegetable oil refining facilities. Sewage sludge as an adsorbent is also effective for the elimination of phosphorus, hydrogen sulfide, boron, fluorides, perchlorate, glyphosate, mercury, arsenate, lead, selenium and other micro-pollutants from wastewater [67, 119-124]. The removal of PAHs (phenanthrene and pyrene) has been reported by using bio-char produced from sewage sludge, with CO_2 as the activating agent for the activation of bio-chars and gives better adsorption activity rather than N_2 [125]. Usage of sewage sludge char is highlighted in Fig.7.

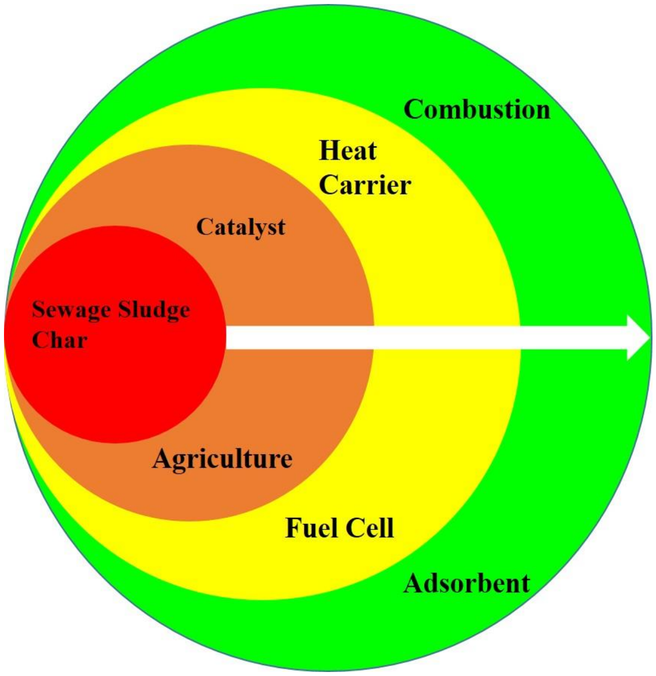


Fig. 7: Usages of sewage sludge char (Sewage sludge is being used in catalyst, agriculture, heat carrier, fuel cell, combustion and adsorbent).

(c) Gases from Fast Pyrolysis

The gas produced from the fast pyrolysis of sewage sludge consists of light gases including H_2, CO, CH_4, C_2H_4, CO_2, C_3H_8, C_4H_{10}. The heating values for bio-oil, char and gas are 32.2 MJ/kg, 12.2 MJ/kg and 24.7 MJ/kg respectively from the fast pyrolysis of sewage sludge at 500°C [126]. The yield of gas would be more at higher temperature pyrolysis for example, up-to 700-800°C. However, as the temperature increases there is a chance of increasing NOx, SOx, tars, PAHs and particulate matter (PM). PM formation during sewage sludge pyrolysis at different gas residence time and 1000°C can increase from 1.14wt.% to 6.33wt.% due to mainly large gas flow rates [127]. The pyrolytic gases have less heating value at lower to medium pyrolysis temperatures but they have the potential to be used for heating purposes.

4.1.3 Kinetics of Pyrolysis for Sewage Sludge

Thermogravimetric analysis (TGA) is the technique commonly used to understand the decomposition mechanism and to determine the parameters of reaction kinetics. Assessments of these mass losses via TGA can be examined at a constant temperature or heating rate. Isothermal TGA is difficult and involves an extensive range of temperatures to determine the mass losses. Non-isothermal TGA has the flexibility to accelerate the analysis of temperatures. Once the thermal conversion scheme is understood via mathematical formulations of the reactions and reactors, then it can be applied to manufacturing applications [128]. TGA has been largely employed to investigate the thermal degradation characteristics of various components such as coal and biomass fuels, including animal manure and municipal and industrial sludge [128, 129]. By using the TGA data along with FTIR, an understanding of the reaction kinetics can be made by using different models. The thermal analysis of TG and DTG data has shown that pyrolysis of sewage sludge involves multifaceted reaction steps.

Researchers have reported three stages of weight loss for TGA analysis of sewage sludge at different temperature ranges: (a) 180-200°C: The loss of water absorbed in the sludge (5-10%), an endothermic reaction. (b) 200-600°C: decomposition of volatiles (main component decomposition and maximum mass loss rate 40-70%), an exothermic reaction. (c) 400-700°C: Decomposition of organic and inorganic materials (9-40%), an endothermic reaction [75, 130-134]. Three mass loss stages at temperatures of 120°C, 130-492°C and 492-720°C during the TGA of sewage sludge under pyrolysis conditions are shown in Fig. 8. The initial weight loss (5%) is related to water removal which is absorbed in sewage sludge. The second weight loss is 66.72% of the total weight loss which is related to the loss of organic volatiles leading to decomposition of constituents including hydrocarbons (between 200-370°C) and proteins, sugars, aliphatic compounds of sewage sludge between 400-600°C. These initial two stages are also shown by the DTG curve: the first mass loss stage at a temperature of 85°C and later stages show two major mass loss peaks at 276°C and 333°C and gradually decreasing in mass until 492°C. The weight loss associated with organic material may continue up to temperatures of 600°C, and between 600-700°C weight loss of inorganic material is observed. Due to the presence of inorganic material for example, calcium carbonate and ash in the sewage sludge, the weight loss is minor between 600-700°C, therefore the inorganic mass loss stage has shown almost constant weight loss in the DTG curve. Hence, the overall weight loss in this third stage is 9%. An endothermic process is shown in the DSC curve which is due to the poly-condensation of C-C bonds and C-O bonds occurring in this temperature range [132]. Thus, the major weight loss is between 200-600°C and activation energies are reported over the range of 125-756 kJ/mol for industrial sewage sludge samples [130].

Different models have been used to calculate the activation energy and pre-exponential factor through differentiation and integration for example, the Coats Redfern model, Doyle equation, Ozawa equation and Freeman-Carroll equation. However, the Coats Redfern approach is reported as the most extensively used model for sewage sludge pyrolysis for the calculation of kinetic parameters [135]. By increasing heating rate and temperature, activation energy would decrease. Likewise, activation energy can also be lowered by using a catalyst [131]. The activation energy for the catalyzed reaction is on the lower side and for un-catalyzed reaction is on the higher side, therefore the rate of un-catalyzed reactions can move towards higher temperature. In Table 8, activation energies and frequency factor / pre-exponential factor (to be used in the Arrhenius Equation), of different pyrolysis reactions of sewage sludge are given in terms of reaction kinetics. As sewage sludge is a heterogeneous material and contains different components depending upon the source, it is difficult to determine all the reactions that may occur during pyrolysis. Consequently, reported results in the literature for kinetic parameters are varied due to the differences in sewage sludge composition and also the use of different kinetic models. In order to find the most suitable model for sewage sludge, linear fitting of the reactions and the linear regression coefficient R^2 need to be known for each model. The most suitable model would have a linear regression near to 0.99, however R^2 cannot show whether the reaction mechanism is a best fit or not. Thus, different models produce different kinetic parameters and it is difficult to state that one model is suitable for all the different reaction mechanisms occurring during sewage sludge pyrolysis.

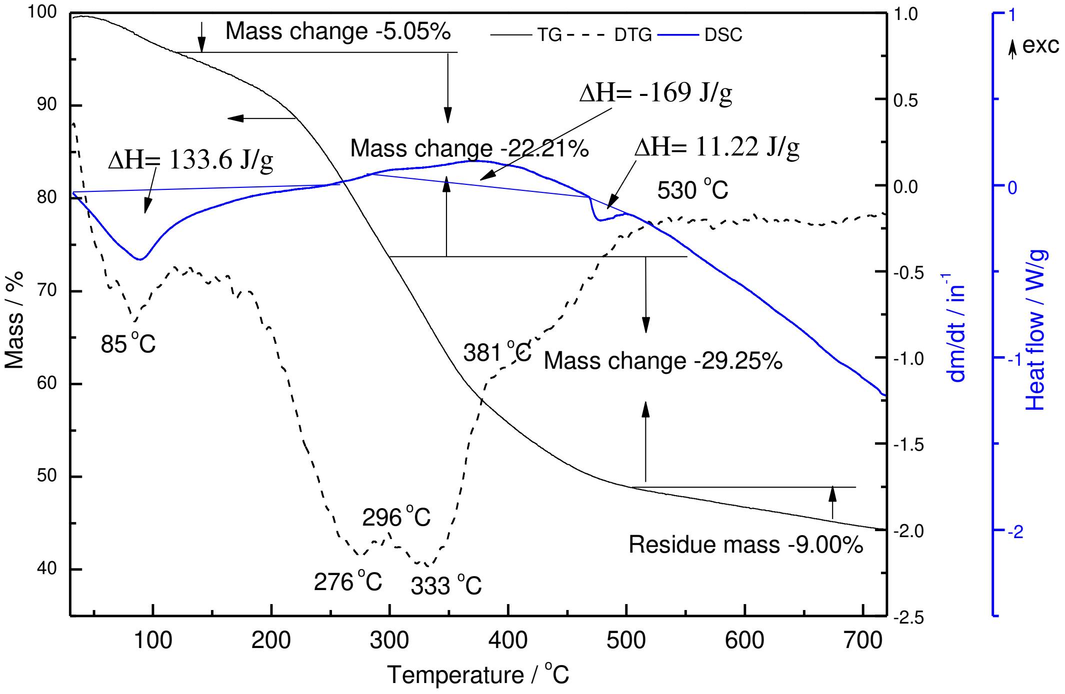


Fig. 8: Weight loss of sewage sludge analyzed on TGA, DSC and DTG [132].

Table 8: Summary of activation energy and pre-exponential factor for sewage sludge pyrolysis.

Heating rate (°C/min)	Temperature range, (°C)	Activation Energy, E (kJ/mol)	Pre- Exponential Factor, A (min-^{1})	Ref.
5	240-330	25.80	47.55	[136]
5	400-550	9.61	44.99	[136]
10	186-296	82.28	$3.55x10^7$	[132]
10	296-518	48.34	$8.04x10^2$	[132]
10	200-385	50.0	2.04	[137]
10	385-510	169.6	3.45	[137]
20	290-400	52.2	$1.3x10^4$	[79]
20	240-330	72.4	$3.63x10^5$	[142]
20	400-600	19.8	3.36	[79]
30	400-600	21.7	7.8	[79]
40	400-600	15.3	2.4	[79]
10	232–489	82.3	$7.7 x10^6$	[135]
15	243–501	95.1	$1.2 x 10^8$	[135]

4.1.4 Co-pyrolysis of Sewage Sludge

In order to improve the quality and quantity of products from the pyrolysis of sewage sludge, addition of other feedstocks to the sewage sludge via co-processing is an interesting approach. The reported feedstocks for co-pyrolysis with sewage sludge include pinewood saw dust [138], microalgae [139], saw dust [140], rice straw [141-143], wheat straw [144], bamboo saw dust [145], manure [146], hazelnut shell [147], cotton stalk [147, 148], oil shale [149], lignite [150], bagasse [151], and wood waste [152]. These feed stocks, enhance H_2, CO and other gas production, increase the surface structure of bio-chars and improve the elimination of oxygenated compounds, water and concentrations of other pollutants in the bio-oil. As can be seen from Fig. 9, biomass like bagasse, rice straw, wheat straw, rice straw and hazelnut shell have more weight loss than sewage sludge in the temperature range of 200-600°C, so in this scenario there is more chance of decomposition of volatile matter and in turn high oil and gas yields. The types of biomass shown in Fig. 9 will have different thermal degradation profiles which will be linked to their differences in macromolecular structure. Biomass consists of mainly cellulose, hemicellulose and lignin and different types of biomass vary in their content of these biopolymers. Each of the biopolymers decompose over different temperature regimes, the first to decompose is hemicellulose in the temperature range 200-350 °C, cellulose decomposes between ranges between 330-450 °C. The low ash content of biomass may add improvement in the characteristics of oil and char and reduce the pollutants in sewage sludge. In Fig. 10, it is shown that the concentration of phenols, ketones, amines, aliphatic hydrocarbon and aldehydes are reduced in co-pyrolysis of sewage sludge and sawdust while there is an increase in acids and esters. By using manure as co-pyrolytic feedstock, there is a decrease in the percentage of phenol, ketone and aldehydes and an increased trend is witnessed in acids and aliphatic hydrocarbons. The gases produced during co-pyrolysis show a high yield of H_2, almost 35% is observed during the co-pyrolysis of sewage sludge and saw dust, while more CO_2 is reported by using manure, wheat straw and pinewood as shown in Fig. 11. As sewage sludge has more nitrogen content than coal, so NOx concentrations may be increased during the pyrolysis of sewage sludge, however, NOx can be reduced by addition of coal. The higher O/N content in biomass results in more NO formation which can be decreased by using high blends of sewage sludge. The addition of coal and biomass can also enhance the synergistic value of co-pyrolytic chars [153-156]. Bio-char produced from the co-pyrolysis add value in terms of specific surface area and HHV. The average HHV of bio-char from sewage sludge pyrolysis is 12 MJ/kg while for lignite it is reported to be 32 MJ/kg with an increased surface area 97.14 m^2/g as illustrated in Table 9. The results may vary depending upon the operating conditions such as initial feedstock size, residence time and temperature and also due to reactor configuration. Thus, co-pyrolysis of sewage sludge can add synergistic value to the produced products. Hence, it is shown that co-pyrolysis can give encouraging results to improve the deoxygenation and heating value of bio-oil, to reduce the nitrogen, sulfur and other pollutants and to enhance the heating value and specific surface area of chars.

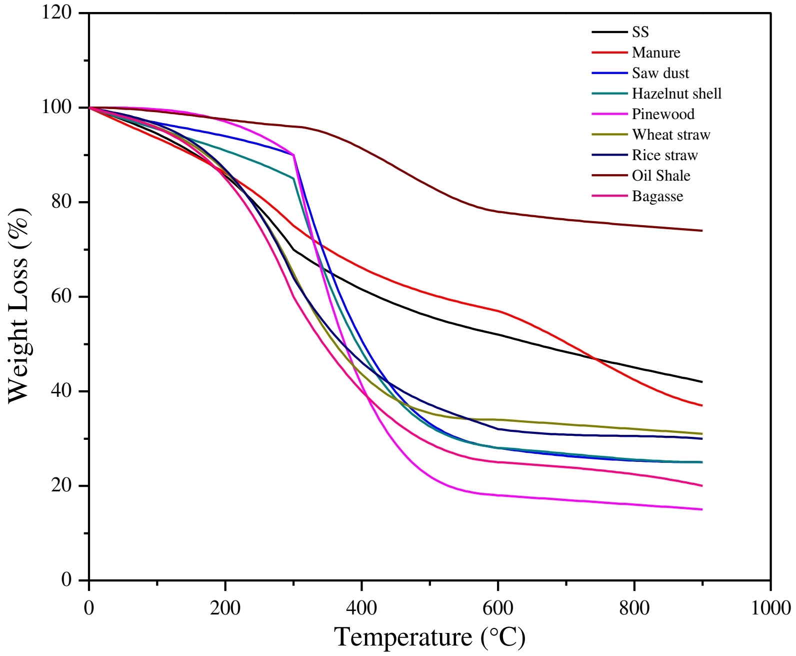


Fig. 9: Comparison of weight loss of sewage sludge and co-pyrolytic feedstock's through TGA [138] [140-145] [146] [147] [149] [151, 152].

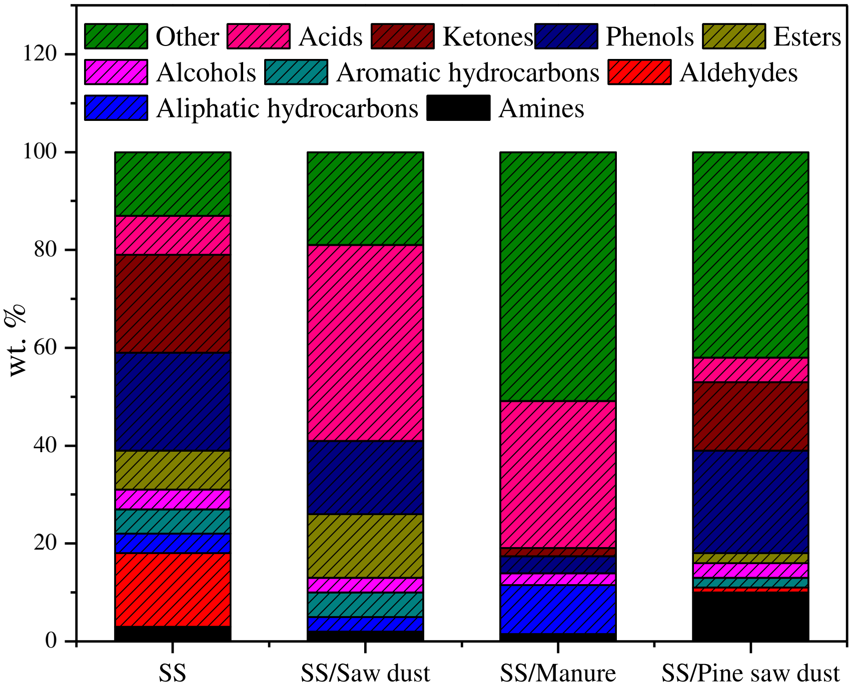


Fig. 10: Comparison of chemical species found in co-pyrolytic bio-oil [138, 140, 144, 146].

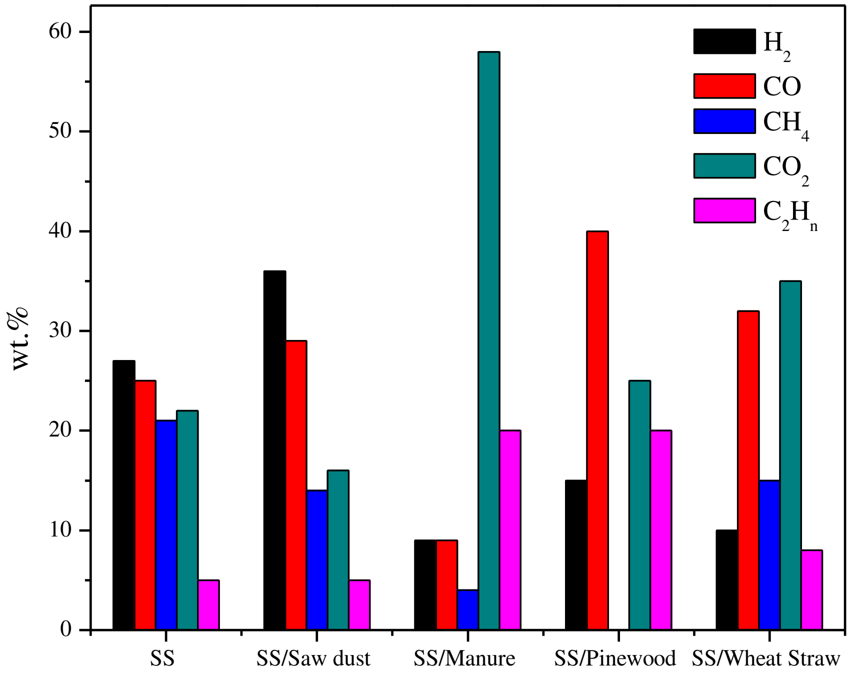


Fig. 11: Comparison of gas yields in co-pyrolysis [138, 140, 144, 146].

Table 9: Characteristics of co-pyrolytic chars using SS and lignite, manure, pine saw dust and rice straw.

Characteristics	**SS[150]**	**SS/lignite[150]**	**SS/MN[146]**	**SS/ PSD[138]**	**SS/RS[141]**
Proximate Analysis					

Moisture (wt.)	-	-	-	-	44.3^{b}
Volatiles (wt.%)	-	n. t	19.5	19.7	41.7^{b}
Fixed Carbon (wt.%)	-	2.86	18.2	29.6	2.6^{b}
Ash (wt.%)	100	97.14	62.2	50.7	55.7^{b}
BET Surface Area (m^2/g)	12.75	32.14	n. t	30.7	6.6
HHV (MJ/kg)	n. t	n. t	11	12.6	n. t

b=dry basis, n. t= not tested, MN= manure, PSD= pine saw dust, RS= rice straw.

4.2 Catalytic Pyrolysis of Sewage Sludge

Catalytic fast pyrolysis is a combined process for generation of liquid fuel which contains high energy content and is able to be used for heat, power, biofuels and chemicals. This technology has emerged as an environmentally sustainable option in terms of versatility and high efficiency. In comparison with co-pyrolysis, the use of catalysts is challenging due to coke formation on the catalyst and catalyst regeneration issues. However, many studies have shown that addition of a catalyst or additives can improve the value of the end-products. The catalyst can be added at three stages, before pyrolysis (as a conditioner), during pyrolysis (in-situ) or after the pyrolysis to reform the volatile vapors (ex-situ). The properties of products are varied by changing the catalyst type to obtain diverse product distributions in altered operating conditions. In many studies, it has been observed that if the catalyst is not used effectively with the optimum operating conditions. The sewage sludge would cause catalyst coke formation, giving only a nominal amount of bio-oil. In relation to sewage sludge, researchers investigating catalytic pyrolysis have worked not only to enhance the bio-oil properties but also to improve hydrogen production and removal of nitrogen, sulfur and chlorine. In order to obtain high oil yields, optimum reaction conditions are required to sustain oil production and reduce bio-oil exposure to the lower temperatures that are favorable to the formation of charcoal. Nevertheless, deactivation of catalyst due to coke formation on active sites and catalyst sintering in the case of high temperature pyrolysis is a problem. Fig.12 illustrates the mechanism for use of catalyst and coke formation.

An analysis gained from different researchers concludes that pre-treatments of sewage sludge before pyrolysis can give enhanced homogeneity of the bio-oil. The role of a catalyst in pyrolysis is to produce a higher quality of the desired product which can be either gas, char or bio-oil, but mostly bio-oil is the desired product. In the gas phase more hydrogen and carbon oxide yields are required with suppression of pollutants especially at high temperature pyrolysis. The aim of bio-oil upgrading has five main objectives: (1) to increase the carbon and hydrogen yield, (2) to lower the oxygen and water content, (3) to increase the quality of bio-oil in terms of higher heating value (HHV), (4) to lower the viscosity and (5) to reduce the pollutants. Catalytic pyrolysis is used to obtain these five objectives and thereby to stabilize the storage value of bio-oil. In this regard, a limited range of catalysts have been studied for pyrolysis of sewage sludge. Consequently, the important factors required for catalytic pyrolysis are; (a) use of additive or conditioners in a first stage to improve the moisture content. (b) use of catalyst to reform or crack the volatile vapors from pyrolysis to produce high quality bio-oil and (c) to examine the effect of metals supported on zeolites, alumina, metal oxides, sewage sludge char and activated carbon to reduce the pollutants.

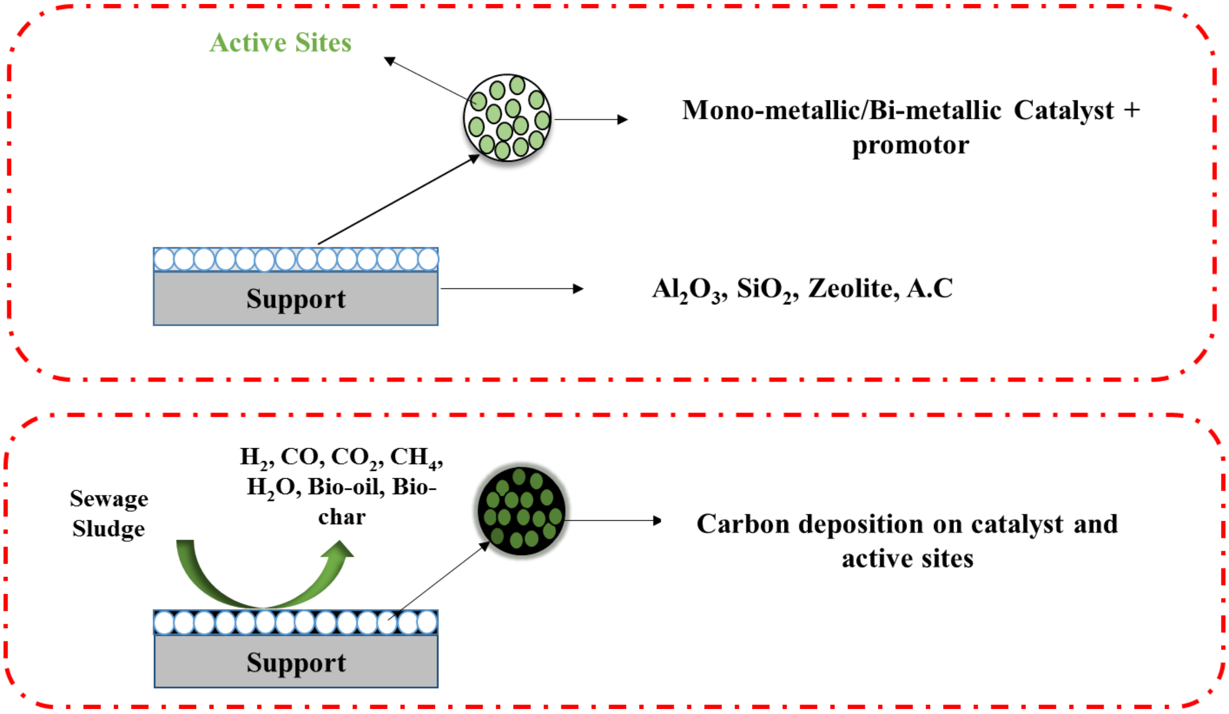


Fig. 12: Catalytic fast pyrolysis and coke formation.

4.2.1 Catalytic Effect of Metal Oxides

It is evident that sewage sludge has a high nitrogen and moisture content. To tackle this problem many researchers have used different types of catalyst/additives, for example, CaO as a conditioner to reduce water content or mixed with metal oxides in combined form to act as a catalyst. However, the energy efficiency of pyrolysis processes also depends on prior dewatering and drying. Metal oxides including, Al_2O_3, CaO, Fe_2O_3, TiO_2, and ZnO have been investigated with sewage sludge pyrolysis. The existence of Fe_2O_3 and ZnO may create possibilities to prevent the degradation of organic matter in a demineralized sewage sludge sample to produce a high amount of solid residues, while Al_2O_3, CaO, and TiO_2 are favorable to promote the decomposition of organic matter and to produce more liquid. It is clear that metal oxides stimulate the preliminary breakdown of the sludge sample. Pyrolysis reaction time with Al_2O_3 and TiO_2 is less than CaO, Fe_2O_3, and ZnO, CaO, TiO_2, and ZnO are also able to change the structure of the demineralized sewage sludge sample. Overall, it may be concluded that TiO_2 and Al_2O_3 has a clear positive impact on sewage sludge pyrolysis. The gamma form of alumina (γ-Al_2O_3) is effective for the production of a single organic phase instead of two phases (organic and aqueous) with enhanced bio-oil properties of stability, viscosity, HHV and composition. Furthermore, composite catalysts containing alumina can decrease the oxygen content of bio-oil by increasing secondary cracking reactions, however high alumina content can lead towards aromatization. Active metals can be added in to these metal oxide supports for the reforming of volatile vapors by using Ni/Al_2O_3 to convert the NOx produced from sewage sludge into N_2 and to produce clean gas enriched in H_2 (68 vol.% at 650°C) [157]. Moreover, Fenton's reagent and red mud as a conditioner have influence on high temperature pyrolysis to improve the H_2 yield. Fenton's reagent and CaO also produced the same results, nevertheless iron can transform tar into more gas whilst CaO leads to more C-OH, C- (O, N) in char. Another advantage of Fenton's reagent is the capture of sulfur in char at up to 97%. Red mud is an alkaline industrial by-product formed in the alumina extraction process from bauxite leaching with sodium. Its chemical composition includes Fe_2O_3, Al_2O_3, SiO_2, TiO_2, Na_2O and CaO. As sewage sludge has a high level of metallic oxide, Red Mud makes a promising catalyst for the pyrolysis of sewage sludge for the production of bio-oil. The catalytic effect of CaO is also encouraging for the conversion of NOx precursors into N_2 for sewage sludge pyrolysis. Researchers suggested that calcium carbon-nitride and decomposition to CaCx is the mechanism responsible to remove nitrogen from sewage sludge. On the other hand, KCl is effective in the reduction of PAHs with a reported reduction from 15.3µg/g to 4.23 µg/g at 850°C as compared to CaO, Na_2CO_3 and Fe_2O_3 [158]**.** While use of CaO can lead to decrease PAHs in bio-oil. CaO and La_2O_3 together results in a slight decrease of oil yield but a substantial decrease in chlorine content from 498-293 ppm [159]. $FeCl_3$ and lime pretreatment can also better transform the thermal degradation profiles of sewage sludge pyrolysis in terms of nitrogen and phosphorous. Sewage sludge contains phosphorous which consists of both inorganic and organic elements having orthophosphate mono-esters and di-esters. On addition of CaO in sewage sludge, orthophosphate di-esters convert to mono-esters and inorganic elements leads to hydroxylapaptite which is a potential phosphorus source for plants as presented in Fig.13. This phenomenon is totally dependent on the temperature, at high temperature organic fractions converted to inorganic fractions having more ash content. Consequently, using metal oxides not only help to improve the moisture content, synergistic bio-oil and clean gas enriched in H_2 but also are promising in effective transformation of nitrogen and phosphorus. Therefore, use of metal oxides to enhance the product properties has been shown, but deactivation of the catalyst with high temperature pyrolysis needs more detailed study.

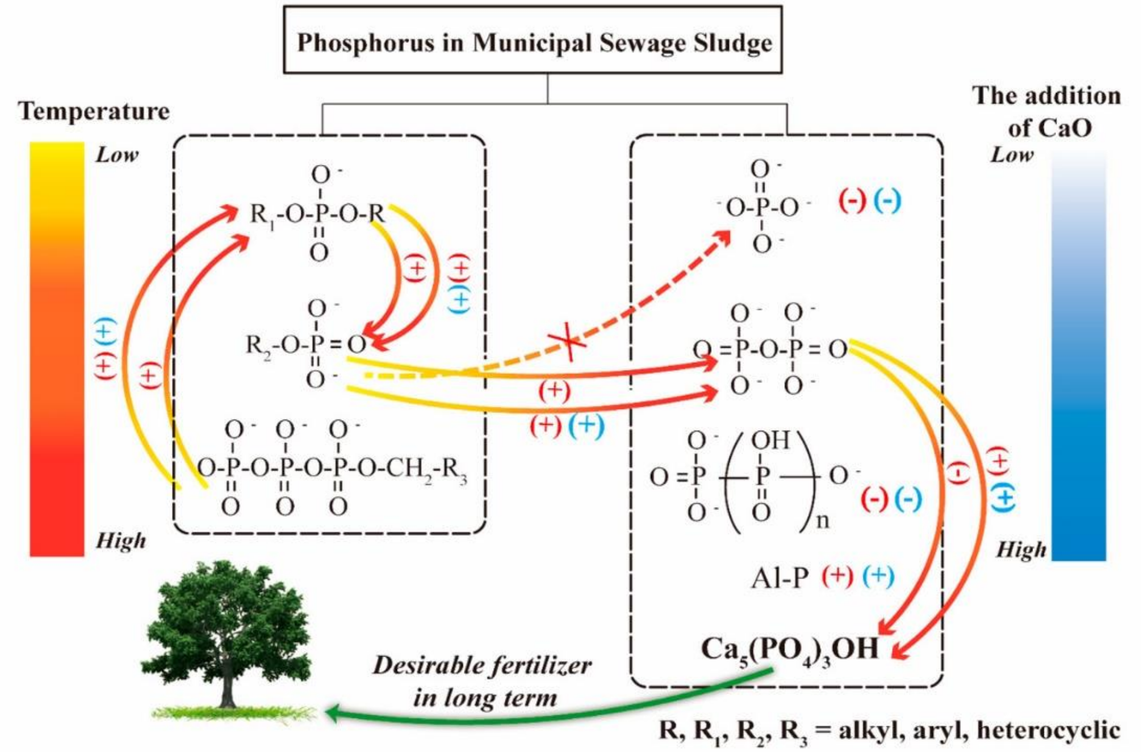


Fig. 13: Illustration of P recovery with addition of CaO [160].

4.2.2 Catalytic Effect of Zeolites

Sewage sludge contains proteins and in excess produces a highly viscous bio-oil during pyrolysis having more oxygen and nitrogen. In this regard, HZSM-5 zeolite has been reported to be effective in the catalytic pyrolysis of sewage sludge for the production of hydrocarbons from pyrolysis vapors due to its properties of deoxygenation, denitrogenation and selectivity [161-163]. It has been shown that, acid pretreatment of sewage sludge is beneficial for the removal of ash content and to avoid catalyst deactivation, whilst HZMS-5 also helps to promote a bio-oil with a higher content of aromatic compounds, deoxygenation of the product bio-oil and N_2 production from NH_3 with delayed deactivation of catalyst [162, 164, 165]. It has been reported that increasing the amount of SiO_2/Al_2O_3 in HZMS-5 resulted in lower concentrations of aromatic compounds in the bio-oil at same operating conditions. Another experiment reported less oil and char yields and higher gas yields by using HZMS-5 with SiO_2 only (no alumina).

The catalysis temperature and pyrolysis temperature play an equally important role in the formation of aromatic compounds. Similarly, use of USY zeolite helps to reduce the activation energy and to promote the decomposition of volatile matter for higher oil and gas production [131]. HZMS-5 has the capability to break the C-C bond especially in nitriles and leads to the production of aromatic compounds and ammonia. HZMS-5 cracks the pyrolytic vapors into intermediates due to having large pore size and a three-dimensional structure. Addition of metals with HZMS-5 can improve the generation of intermediates to produce clean gas and oil. However, addition of metals on HZMS-5 can also decrease the specific surface area and pore volume due to very small particle size. So, there should be proper dispersion of metals on supports to expose more active sites to reactant vapors and to generate more intermediate products. During catalytic pyrolysis, by using the transition metals Ni and Co on HZMS-5, macromolecules of amines in sewage sludge might crack in to smaller molecules due to the acidic sites present in zeolites and generation of H radicals with dehydrogenation, dehydration and deamination. A reaction pathway is given in Fig. 14 for the N transformation. Ni and Co are known for the cleavage of C-C bonds by transforming HCN to NH_3. The constraint of coke formation on active sites cannot be ignored because at high temperature Ni is more prone towards coke formation. In this regard, other bimetallic combination with zeolites can also be studied. The combination of Mo-Co, Mo-Ce, Ni-Mo, Mo-Ce, Ni-Ce can also be tested, as researchers have studied these bi-metallic catalysts for biomass and other wastes. There is lack of detailed studies, based on coke formation and regeneration of catalysts during the N and P transformation of sewage sludge catalytic pyrolysis.

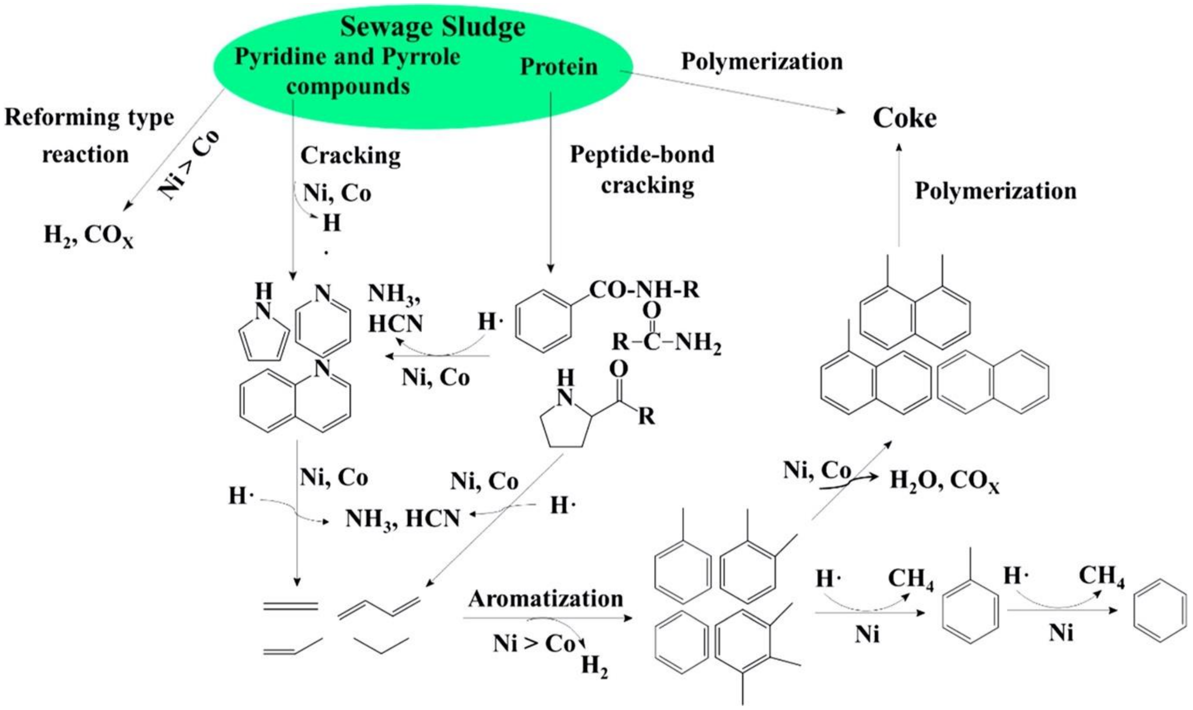
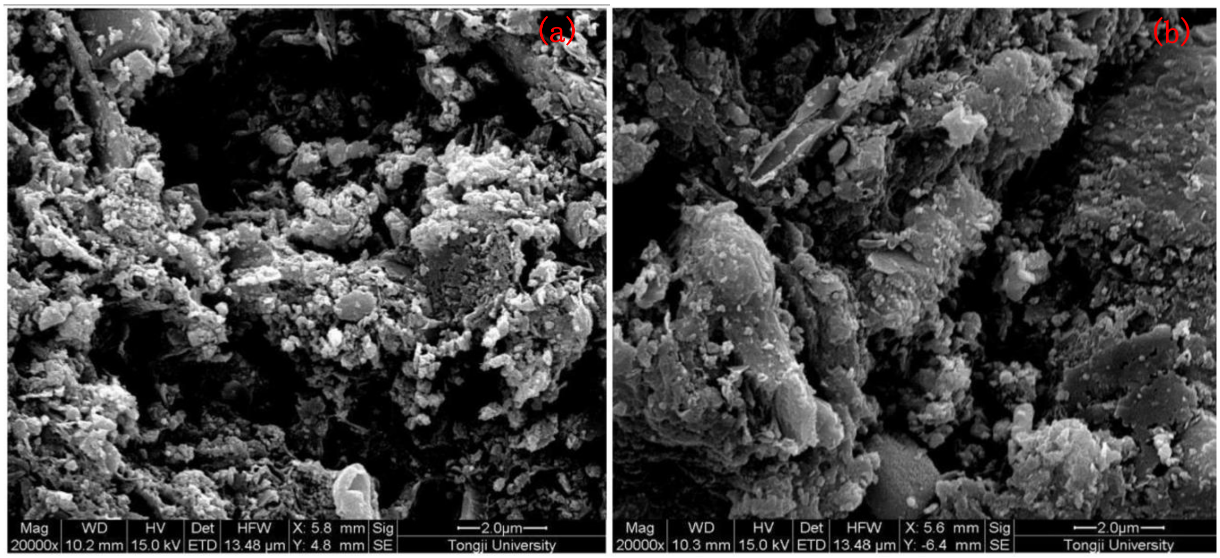


Fig. 14: Reaction pathway for catalytic pyrolysis by using Ni-Co/HZMS-5 [165].

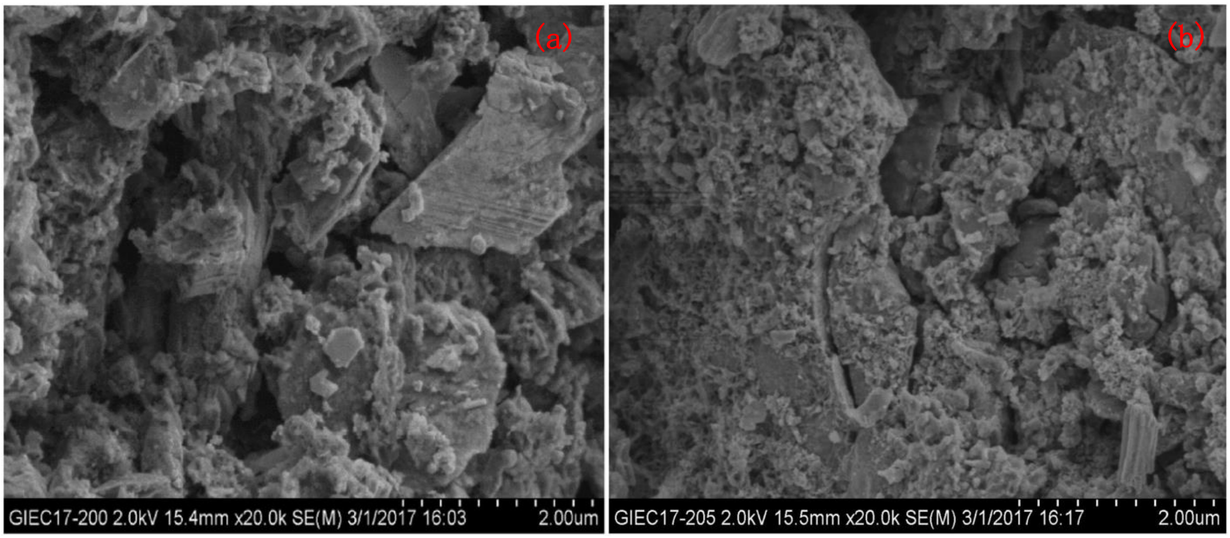
4.2.3 Catalytic Effect of Sewage Sludge Derived Char

Recently, the use of sewage sludge derived char has been widely studied, for example, the generation of sewage sludge char has shown promising results in the reforming of pyrolytic vapors. The sewage sludge characteristics of heavy metal provides enough inorganic fractions including Mg, Na, Ca and K to promote the catalytic activity and the char produced at higher temperatures have higher surface area and pore volume and in turn higher activity to reform the pyrolytic vapors and tars. In order to examine the catalytic role of sewage sludge, char has been investigated by researchers with encouraging results. Sewage sludge char impregnated with activation agents such as KOH and $ZnCl_2$ are promising for reducing NOx, in addition, activated carbon can also be produced. Comparison of char with dolomite and quartz, show that char has more effective reforming efficiency to produce bio-oil with less oxygenated compounds and nitriles, and improved heating value of the product gas [166]. Addition of active metals on sewage sludge char gives enhancement in the catalytic activity for improved results compared with metal oxides and zeolites [167, 168]. The dispersion of metal on char can augment the surface area and pore volume but during reforming the fixed carbon present in the sewage sludge and hydrocarbon oil content may cover the active metal pore sites which leads to coke formation and deactivation. This phenomenon is shown in Fig. 15 (a) and (b) by SEM images before and after reforming of pyrolytic vapors on sewage sludge char and Fe embedded sewage sludge char. Therefore, it is most important to know the dispersion of metals towards coke formation and the thermal stability of the catalyst support material. The deoxygenation of bio-oil on Ni, Co, Mo, Zn, Fe, Cu, Cs, Mg and noble metal based catalysts with various support materials has shown promising results for sewage sludge [169]. A summary is presented in Table 10, to highlight the catalytic effect on oil and gas yields, HHV's and reduction of pollutants for example NOx, SOx and PAHs.

The use of sewage sludge char either combined with active metal or not, is suitable for catalytic purposes because it is easy to generate, easy to use torrefied and carbonized char and most importantly it has low cost. Researchers have upgraded the bio-oil from biomass via dehydrogenation by using mono and bi-metallic sulfide catalyst supported on zeolites, metal oxides and activated carbons under certain pressure such as fluid catalytic cracking of fossil fuels. However, such kinds of catalysts and processes have not been reported for sewage sludge extensively. The reasons might include: (1) Sewage sludge has high ash content which is a great limitation for using expensive catalyst combinations. (2) Due to sewage sludge containing proteins, amines, phosphorous and other pollutants, resource recovery has the same importance along with producing synergistic products. (3) Preparation of metallic catalyst needs calcination and consideration of regeneration issues after the reforming process. Due to the high ash content of sewage sludge, deactivation of metal catalysts would be increased. Therefore, a range of catalysts need to be studied in depth with sewage sludge as the feed stock for enhancement of pyrolytic products.



SSC



SSC+3.5%Fe

Fig. 15: SEM images of sewage sludge char and Fe- embedded sewage sludge char (a) before reforming (b) after reforming [170].

Table 10: Summary of the catalysts used in the catalytic fast pyrolysis of sewage sludge.

Feed Size	Catalyst	Preparation Method	Temp. °C	Observations	Ref.
106-125 μm	Al_2O_3, CaO, Fe_2O_3, TiO_2, and ZnO	The metal oxides were calcined at 1073 K for 2 hr.	800	TGA study was conducted to observe the weight loss of different metal oxides with sewage sludge. Al_2O_3 and TiO_2 and CaO have shown good results to restrict char production.	[106]
250-500 μm	γ-Al_2O_3	γ-Al_2O_3 ex-situ calcined at 600°Cfor 3 hr. and kept in desiccator.	600	It was observed that a slight decrease in oil yield but improved organic phase with better HHV, stability and viscosity was caused by post treatment with catalyst.	[171]
0.25-0.6 mm.	Composite alumina	Composite alumina was formed by alumina particles having 0.3–0.5 mm diameter 850°C.	600	By using composite alumina the highest yield of liquid was around 48.44 wt.% and while changing the temperatures the yield of products produced less aromatics and more aliphatic compounds.	[172]
<250 μm	Ni/Al_2O_3	Ni loading 20 ± 2 wt.%, 0.5-1.0 mm	650	High yield of H_2 68vol.%. It was observed that improvement was caused by Ni/Al_2O_3 for bio-oil reforming and prevented coke deposition. NOx converted to nitrogen and 20% remained in char.	[157]
180-250 μm	S-Fenton-CaO	S-Fenton was prepared by adding water, sulfuric acid and $FeSO_4$ and H_2O_2, all were well mixed. S-CaO was prepared by mixing of water and CaO.	600	Hydrogen yield was increased by using combination of two conditioners and provision of Fe_2O_3, CaO. Ca and Fe helped to convert tar into more gas. Only Fenton treatment captured the sulfur in char up-to 97%.	[173]
75 μm	Fenton's reagent and red mud	Fenton’s reagent (32 mg Fe^{2+}/g dry solid (DS) combined with 34 mg H_2O_2/g DS) and red mud (275 mg/g DS).	700	Red mud with more Fe_2O_3 content promoted enhancement of the H_2 yield by decreasing the tar. Aromatic nitriles, mono aromatics and PAHs were 10%, 4.96% and 54% by weight at 700°C.	[174]
60 μm	CaO,KCl,Na_2CO_3, and Fe_2O_3	Metal oxides were calcined at 1073K for 2 hr.	850	It was found that catalysts have ability to restrict PAHs at higher temperature. The concentrations in bio-oils were 14, 4, 4 and 8 μg/g with non-catalyzed, KCL, Na_2CO_3 and Fe_2O_3.	[158]
0.4-1.0 mm	HZSM-5 with SiO_2/Al_2O_3	HZSM-5 with the SiO_2/Al_2O_3 ratio of 25, 50, and 80 The catalysts sieved to 0.4 to 1.0mm and activated in air at 550 °C for 5 hr.	500	HZSM-5 with Si/Al ratio of 25 gave 16.4% yield of aromatics and enhanced the transformation of nitrogen to NH_3. HZMS-5 proved to break the C-C bonds of amines macro molecules.	[175]
1 mm	ZSM-5	ZSM-5 was activated at 550°C for 4 hr.	600	At 550°C, the highest yield 41.39wt% of bio-oil was attained by using ZSM-5 catalyst. HHV’s of gas and oil were 22.5 MJ/Nm^3 and 20.61 MJ/kg.	[113]
<75 μm	HZSM-5	HZSM-5 was calcined at 600°C for 5 hr.	600	Full retrieval of inorganic elements were found in the char, which suggests that catalyst deactivation maybe lessened through ex-situ catalytic pyrolysis.	[161]

0.45 mm	SiO_2-Zeolite	A zeolite (SiO_2) without alumina was blended with 5g of dried sludge.	500	Pretreatment with acid or base did not help to enhance the bio-oil quality. The gas yield was approximately 9–20% and the energy loss was less than 10% over the range of sludge types. More oil yield was observed in primary sludge rather than digested sludge.	[176]
75 µm	KOH and $ZnCl_2$ over SS char	The solutions of $ZnCl_2$, $Fe(NO_3)_3$, and $Mn(NO_3)_2$ were blended for 2 hr with SS. The KOH to sludge mass ratio was 1:1 and the samples were dried for more than 24 h in an oven at 105°C.	700	Results showed that activation agent impregnation with SS char could be an environmentally friendly and energy-saving approach for the production of activated char and also for De-NOx.	[177]
250 µm	Fe-embedded SS char	$Fe_2(SO_4)_3$ added in wet SS and stirred for 30 min, then dried for 12 hr.	600	Increased gas yield: 15.9-35.8wt%, decrease in liquid yield: 31.9-10.2wt%, increase in HHV of syngas: 12.5-17 MJ/kg and increase in pollutant gases.	[170]

4.3 Reactors for Pyrolysis of Sewage Sludge

An important factor for catalytic fast pyrolysis is the type of reactor used for the process which can represent around 10 to 15% of the overall cost. The reactors which are being used frequently and recommended by many researchers for pyrolysis are fixed bed reactors, bubbling fluidized bed reactors, circulating fluidized beds, rotating cone reactors, spouted bed reactors, ablative reactors, vacuum reactors and screw or auger reactors [178]. In the context of pyrolysis, one reactor is enough to produce the products. Nevertheless, in catalytic fast pyrolysis a second reactor is required to reform or crack the pyrolytic vapors in the presence of the catalyst to produce the targeted products. A two-stage fixed bed reactor is most suitable for such a kind of pyrolysis. In the two-stage reactor system, the first stage is used for pyrolysis of the sewage sludge generating the pyrolysis vapors and gases which pass directly to the second stage containing the catalyst for catalytic reaction. This configuration is developed at the laboratory scale but there is no example at commercial level.

The reactors extensively used for thermochemical processing of sewage sludge are fixed bed, bubbling fluidized bed, auger reactor and rotary kiln and also a few have used circulating fluidized beds. Circulating fluidized bed reactors are favorable for commercial usage in catalytic pyrolysis in terms of catalyst regeneration. In the case of in-situ catalytic fast pyrolysis, short residence times are found, which in the case of fluidized bed reactors, the velocity of the carrier gas flow is very critical with respect to sewage sludge coming from the inlet, so that an optimum contact time between catalyst and sewage sludge particles is produced. To obtain a large quantity and quality of bio-oil, the particle size of the feedstock is important, where high surface area and good heat transfer are favored. Catalyst surface area (support and promoter) also plays a vital role. Moreover, in continuous systems the catalyst regeneration also needs to be considered. The presence of char in the regenerator would create a problematic situation, so the contact time needs to be optimized. It has also been shown that to obtain optimum heat transfer rates, the use of sand as an inert bed material is preferable. In the case of ex-situ catalytic fast pyrolysis, the first reactor which is commonly a fluid bed, an auger reactor or a rotating cone reactor, are used for the preliminary conversion of sewage sludge in to hot pyrolysis vapors. A second reactor is then used for the catalyst, which is commonly a fixed bed or circulating fluidized bed reactor to upgrade the pyrolysis vapors into bio-oil [179]. Consequently, using a two-stage reactor (sewage sludge in the first stage and catalyst in the second stage) is preferable, allowing reforming or cracking of the evolved pyrolytic vapors.

4.3.1 Technological Strength and Market Competitiveness of Pyrolysis Reactors

Coal and biomass are the most extensively studied feed stocks for pyrolysis, so using the same scenarios and equipment can be assumed for other solid wastes like sewage sludge. The suitability of pyrolysis reactors for biomass can be well suited for sewage sludge, the only difference being in terms of feed stock characteristics which need to be characterised. However, these qualities of biomass pyrolysis reactors need to be analyzed before using sewage sludge. Specifically, for sewage sludge Table 11 gives an indication of the properties of different reactors based upon feed size requirement, gas flow rates, bio-oil yields, heating methods, heat transfer rates, scale up capabilities and residence times. The Table shows qualitative data for pyrolysis reactors which can be described quantitatively to discuss their technological strength and market competitiveness. In bubbling fluidized bed reactors, the bio-oil yield is around 75% and can be scaled up to a larger scale easily, but they require large flow rates of gas. Circulating fluidized bed reactors can handle almost the same feed size range as bubbling fluidized bed reactors, however larger gas flow rates would lead to increased complexity and complex systems results in elevated costs. Spouted bed reactors are similar to bubbling fluidized bed and circulating fluidized bed reactors but having a spout shape. The spouted bed geometry produces a cyclic movement of the bed particle material and enables stable operation over a wide range of gas flows. In the case of auger reactors, the feed size can be up to 5mm, which can be handled with low gas flow rates and less complexity. These attributes may vary from case to case, however several researchers have reported the operational results and are shown in Table 11.

Table 11: Qualities of fast pyrolysis reactors.

Characteristics	BFBR	CFBR	SBR	Auger Reactor	Rotary Kiln
Heating methods	Supplied externally to bed/direct or sand [179]	Recirculation of heated sand [180]	Direct/sand[178]	Direct/sand [181, 182]	Direct and indirect [183]
Residence Time	Gas residence time < Char residence time [109]	Gas residence time = Char residence time	Less residence time[111, 138]	Depends on screw speed	Depends on rotation speed and angle
Scale up	Easy	Easy	Easy	Easy	Easy

Feed Size	<2-3mm	Must be less than used in bubbling fluidized reactor	<3mm[111, 138]	5mm	Small, medium and large
Gas Flow Rates	High [178]	High	High	Low	Low [184]
Complexity	High	High	High	Low	Low
Heat Transfer Rate	Good [93]	Good	Good	Good [185, 186]	low
Oil Yield	70-75%	75%	77% [111]	70%	60% [131]

Saaty et al., Vargas et al. [187, 188] and Adar et al. [189] have elucidated how to use Analytical Hierarchy Processes for decision making and how to show the most important and least important factors quantitatively. Table 12 illustrates the quantitative data by using the Analytical Hierarchy Process. The positive attributes are shown in a 10-1 scale value and negative attributes which can cause hindrance in efficiency are displayed from 1-10 scale value. High bio-oil yields are favorable, shown as a 10-1 scale value. High inert gas flow rates, high complexity and hard to scale up of reactors are depicted from 1-10. Table 13 shows the technological strengths for pyrolysis reactors as a sum of all scale values.

Table 12: Scale values for technological strength of pyrolysis reactors.

Bio-oil Yield		**Feed Size**		**Gas Flow Rate**		**Scale Up**		**Complexity**		**Heat Transfer**	
High	10	Large	10	High	3	Hard	3	High	3	Good	10
Medium	6	Medium	6	Medium	6	Medium	6	Medium	6	Medium	6
Low	3	Small	3	Low	10	Easy	10	Low	10	low	3
Very low	1	Very small	1								

Table 13: Technological strength of sewage sludge pyrolysis reactors.

Reactors	**Bio-oil**	**Feed Size**	**Inert gas**	**Scale up**	**Complexity**	**Heat transfer**	**Technological Strength**
BFBR	10	3	3	10	3	10	39
CFBR	10	1	3	10	3	10	37
SBR	10	1	3	10	3	10	37
Auger	6	6	10	10	10	10	52
Rotary	3	6	10	10	10	3	42

Based on these factors one can decide on the technological strength of a reactor, along with scale up capabilities and with cost factors determines whether it is market competitive or not. The technological strength is critically important for the optimum selection of the reactor type, and if the reactor has more technological complexity it would not be attractive to the market. Large flow rates of inert gas and very small feed size are reasons for high complexity. The bubbling fluidized bed reactor, circulating fluid bed reactor, spouted bed reactor and auger reactor have more or less the same bio-oil yields but due to the lower technological complexity of the auger reactor, it has more market competitiveness as compared to other reactors. Depending upon various operating conditions and origin of feedstock, the results may vary for different reactors. A graphical illustration of this technological strength and market competitiveness is shown in Fig. 16 and a process flow diagram for catalytic fast pyrolysis is illustrated in Fig. 17 based upon the whole pyrolytic process for sewage sludge.

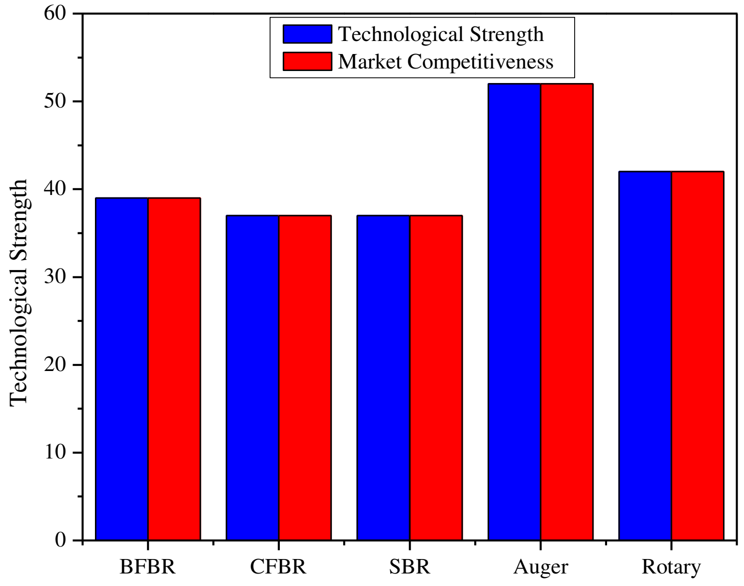


Fig. 16: Technological strength and market competitiveness of sewage sludge pyrolysis reactors.

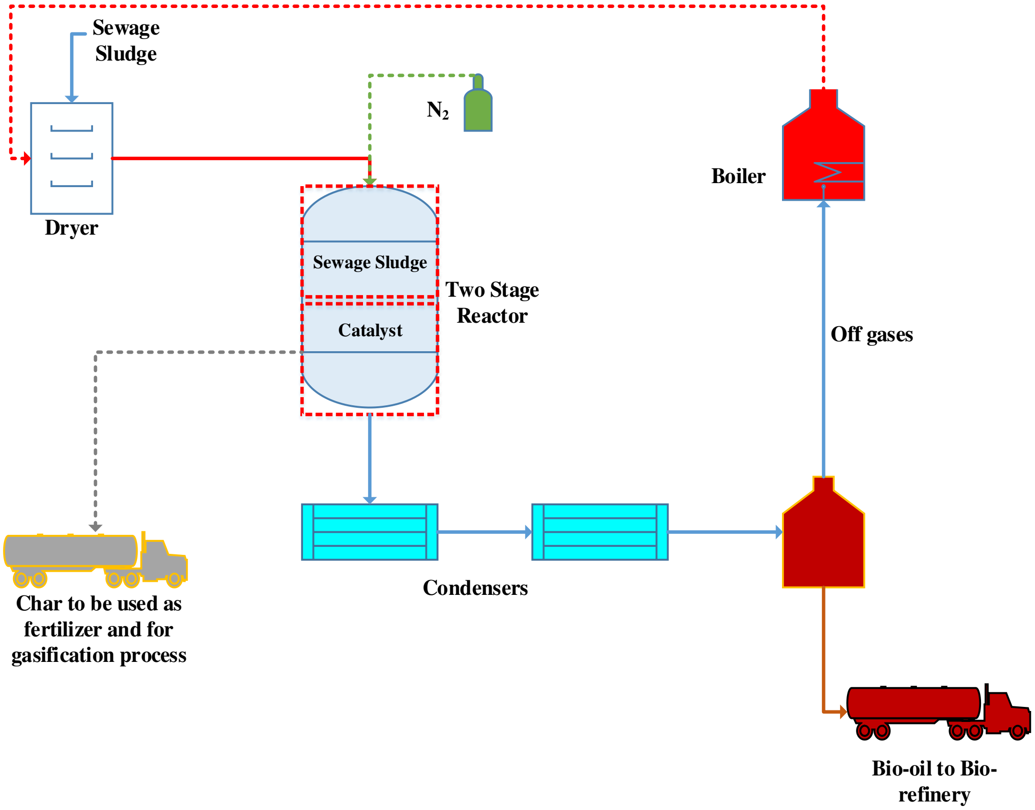


Fig. 17: Process flow diagram of catalytic fast pyrolysis.

4.4 Challenges for Pyrolysis of Sewage Sludge

Using sewage sludge as a waste material for generation of energy and power is an innovative treatment option which has positive socio-economic impacts. Despite the fact that sewage sludge has potential to produce energy, it is also contaminated with heavy metals which can have environmental issues. To cope with such issues, different technologies depending upon requirements are being used. Specifically, towards pyrolysis of sewage sludge, there are a number of challenges to further development: (1) Due to high moisture content in sewage sludge, the product quality is not high. (2) A high amount of energy is required to decrease the moisture content and drying is time consuming while other feeds tocks having less moisture can directly be used. (3) Drying techniques and addition of another feed stock or conditioner have been applied to increase the product value, however deoxygenation and denitrogenation is challenging (4) To enhance the process and product quality only a limited number of catalysts and reactors have been used for pyrolysis so far due to the characteristics of sewage sludge. (5) During production of clean gas and high heating value oil, release of pollutants (NH_3, SO_2, HCl, HCN, PM) and their control is also challenging. (6) Due to high ash content of sewage sludge the catalyst might become deactivated because of coke formation. (7) During deoxygenation, dehydration and denitrogenation of bio-oil, control of reaction conditions with catalysts and reactors is challenging to obtain a quality end-product. (8) The biggest challenge for pyrolysis or catalytic pyrolysis is to make products readily available for direct commercial use.

5. Gasification of Sewage Sludge

Gasification is a known thermochemical method to produce syngas. Syngas is mainly a mixture of hydrogen and carbon monoxide but may also contain carbon dioxide, methane, tar, water and other light hydrocarbons. Torrefied sludge, carbonized sludge, hydro char, pyrolytic char and direct use of sewage sludge in gasification is generally studied. Recently, co-gasification and catalytic gasification of sewage sludge is also under investigation to produce improved quality syngas. Gasification reactions can be carried out at temperatures greater than 800°C and with a partial supply of oxygen. It is normally operated by using air as a gasifying agent, however, many studies have reported using oxygen, steam, CO_2 and mixture of air-steam, O_2-steam, steam-CO_2 as gasifying agents in the gasification process. Although, gasifying agents play a great part in the composition of the final syngas product, however due to the inherent properties of sewage sludge the product distribution and amount of tar and other pollutants may vary substantially.

In order to understand the gasification process, it is important to know the reactions involved. Gasification is sub-divided into four stages which are: (a) Drying (b) Pyrolysis (c) Oxidation (d) Reduction [190, 191]. The drying zone is basically for the reduction of moisture level of the sewage sludge and it is normally in the temperature range of 70-200°C reducing the moisture content to less than 15%. The pyrolysis zone is for the thermal degradation of sewage sludge at temperatures between 350-600°C. Inside the oxidation zone, the residual char and volatiles are oxidized and due to exothermic reactions, the temperature quickly reaches 1100°C. Finally, in the reduction zone, the char is transformed into CO and H_2 by mainly partial oxidation, Boudouard reaction, steam gasification and hydro-gasification. It is observed that, when steam is added to the gasifier the oxidation and reduction zone temperatures decrease and hydrogen volumetric rate increases. A basic gasification reaction is presented in Eq. (1) [191], other basic chemical reactions and mechanisms of gasification are given below in Table 14. Along with the syngas, the pollutant gases from sewage sludge may release as gasification occurs at higher temperature. Moreover, the solid ash may contain heavy metals and consequently they would affect syngas cleaning from tar and ash. To obtain a clean syngas for downstream utilization, several problems have been highlighted such as tar formation which can be prevented by using optimum operating conditions, co-gasification, an appropriate catalyst and suitable reactor system, which are discussed in the next sections.

$$\mathbf{SS \rightarrow CO(g) + H_2(g) + CO_2(g) + CH_4(g) + Tar(l) + H_2O(l) + H_2S(g) + NH_3(g) + C(s) + \text{trace species}} \qquad \textbf{Eq. (1)}$$

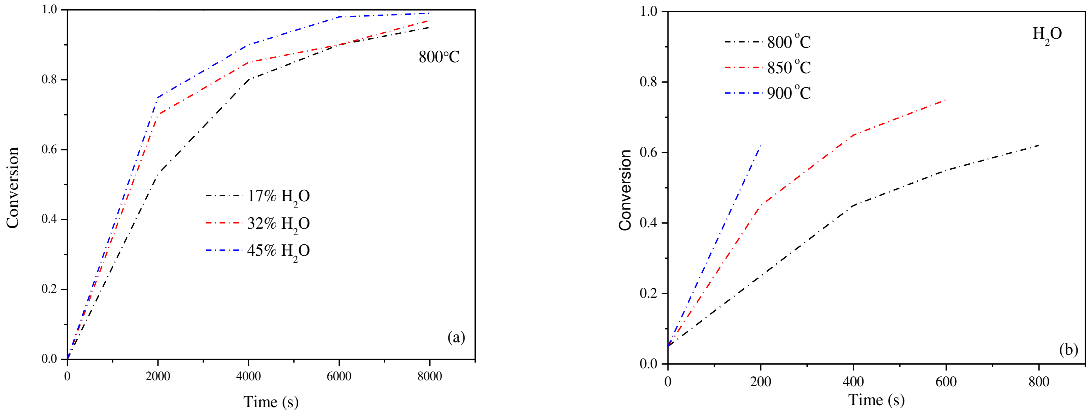
Table 14: Basic chemical reactions and mechanisms for gasification of sewage sludge [26, 192-196].

Reaction Name	Reaction	Endothermic/ Exothermic	Heat of Reaction	Temp. °C	Activation Energy (kJ/mol)
Drying/De-volatization					
	SS + Heat → char + volatiles + water + light gases + primary tar	Endothermic	-	-	
Secondary Tar Cracking					
-	Tar + $H_2O \rightarrow H_2 + CO$	Endothermic	-	-	
-	Tar + $H_2 \rightarrow$ light hydrocarbons + gases	Endothermic	-	-	
-	Tar + $xH_2O \rightarrow yCO_2 + zH_2$	Endothermic	-	-	
-	Tar $\rightarrow CH_4 + H_2 + H_2O + C_nH_m$	Endothermic	-	-	
Carbon Oxidation					
Boudouard reaction	$C + CO_2 \leftrightarrow 2CO$	Endothermic	162.4 kJ/kmol	>700	200-250
Water gas primary reaction	$C + H_2O \leftrightarrow CO + H_2$	Endothermic	131.3 kJ/kmol	>700	143-237
-	$C + 2H_2O \leftrightarrow CO + 2H_2$	Endothermic	14.5 kJ/mol	-	
Combustion of char	$C + O_2 \leftrightarrow CO_2$	Exothermic	-	-	29
Methane decomposition	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	Endothermic	206.3 MJ/kmol	>500	
-	$CO + H_2O \leftrightarrow CO_2 + H_2$	-	-	-	
Shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	Exothermic	-42 kJ/mol	300-600	
Steam reforming reaction	$C_nH_m + 2nH_2O \leftrightarrow (2n + (m/2))H_2 + nCO_2$	Exothermic	-	>700	
Water gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$	Exothermic	-42.1 MJ/kmol	300-600	
Methane Reforming					
Methane formation	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	Exothermic	-221.0 kJ/mol	300-600	

-	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$	Exothermic	-223.0 kJ/mol	300-600

5.1 Kinetics of Sewage Sludge Chars During Gasification

The reaction kinetics of pyrolysis and gasification are not the same; pyrolytic kinetic studies consists of more complex steps than gasification. In the gasification of sewage sludge, char acts as a limiting reactant, because it has to react with steam or carbon dioxide which is a slower step than devolatilization and reforming reactions of the gas phase. As sewage sludge char has more surface area due to its catalytic nature, so the reactivity might be higher than some other waste feed stocks. Whilst in gasification, the reactivity is also dependent on other factors such as the gasifying agent, heating rate, temperature, surface structure of chars, catalyst and other feedstock (if used). The activation energy for the Boudouard reaction and water gas reactions is higher than the initial combustion of char as shown in Table 14. To analyze the reactivity of char, kinetic parameters i.e., activation energy and pre-exponential factor as a function of temperature, heating rate and degree of conversion are important to know. Process temperature has a substantial effect on sewage sludge gasification. Researchers have conducted kinetic studies for sewage sludge to observe the char reactivity and conversion under CO_2 and H_2O gasifying media using TGA at 800-900°C [195, 197]. The char reactivity can be conceived as steam reacting more effectively producing hydrogen in the water gas shift reaction rather than CO_2 as shown in Fig. 18. The char reactivity towards steam is higher at lower temperature and concentrations while conversion with CO_2 needs higher temperature and higher concentration. It has also been seen that evolved gas composition is not much affected by the gasifying media. Based on the data taken from the char conversion, rate constants can be calculated for further activation energy and frequency factor calculations depending upon which kinetic model is being used.



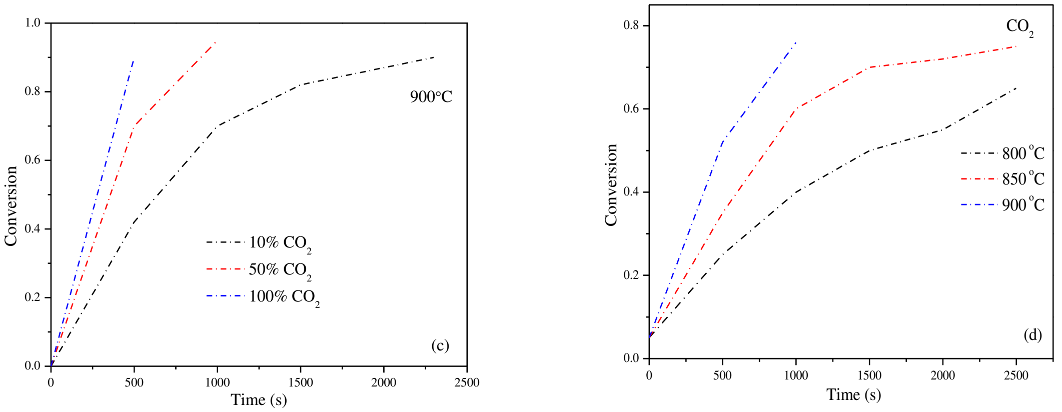


Fig.18: Conversion of char by using H_2O and CO_2. (a) effect of steam concentration at 800°C (b) temperature effect of steam. (c) effect of CO_2 concentration at 900°C. (d) temperature effect for CO_2.
(a) and (c) [195], (b) and (d)[197].

5.2 Reactors for Gasification of Sewage Sludge

During the gasification process a reactor has vital importance. The reactor systems reported by researchers for gasification of sewage sludge are classified into fixed bed reactors [198, 199], fluidized bed reactors [200, 201], circulating fluidized bed reactors [202-204], rotary kiln [205], auger and plasma reactors [206, 207]. Furthermore, the method used for injection of the gasifying agent into the reactor, for fixed bed reactors defines the gasification type as downdraft (cross draft), and updraft (co-current). The feedstock composition like moisture and ash content also effects the final desired product produced from the reactor. In the updraft gasifier, the sewage sludge is fed from the top of the reactor and air, steam, O_2 or a mixture of these gasifying agents is injected from the bottom of the reactor. The produced gas exits from the side of the top. Studies have shown that, this is less efficient due to contamination of the syngas with higher levels of tar. In the downdraft gasifier, the feed inlet is from the top and the gasifying agent enters at the oxidation zone and the produced gas outlet is at the side of the bottom of the reactor. The downdraft gasifier generates good quality syngas because it has less contamination of tar. Some difficulties such as accumulation of slag and pressure drop inside the fixed bed reactors have been observed. A schematic diagram of an up-draft and down-draft gasifier is shown in Fig. 19.

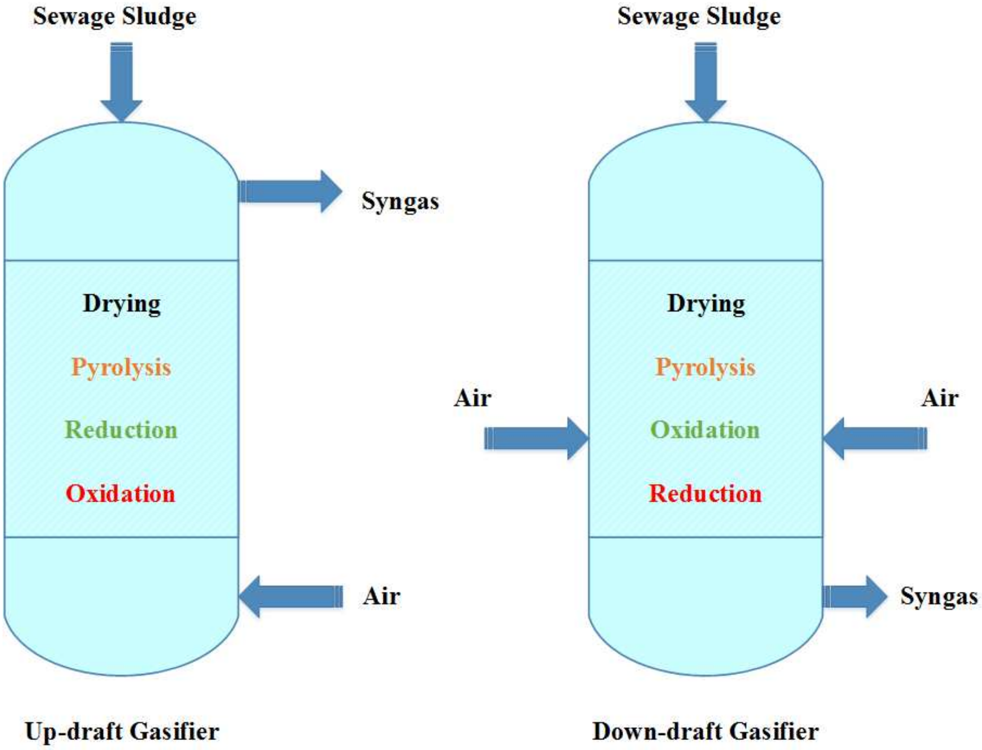


Fig. 19: Stages of gasification in Up-draft and Down-draft gasifier.

Fluidized bed reactors need high flow rates for fluidization of sewage sludge particles and results in high throughputs of the final gas products. They have good heat transfer rates and clean gas can be produced by passing the product gas through cyclones and electrostatic precipitators to extract sand, ash and unburnt char particles. The ash extraction downstream of the fluidized bed reactors is a problematic situation which produces clinker and agglomerates and forms an increased bed height due to the high ash content of sewage sludge. Circulating fluidized bed reactors enable char combustion and regeneration of catalyst (if used). In fluidized bed or circulating fluidized bed reactors there is a possibility of attrition of fuel particles with the high gas flow rates which effect the desired gas quality. Use of high flow rates for fluidization causes problems in handling and maintenance of gasifiers which results in high costs. Therefore, these two reactor configurations have good efficiency in terms of solid gas reactions in gasification, tar removal and syngas quality. In this regard, the two-stage reactor configuration is used to produce a higher quality syngas coupled with ash extraction. Researchers have also reported a three stage configuration to attach one more reactor to the two-stage configuration. The third stage may consist of fixed bed, fluidized bed, auger reactor, rotary kiln or plasma reactor for tar removal and improved syngas quality.

However, this configuration leads to added cost. Auger reactors have also been reported with improved tar removal and syngas quality. Rotary kilns have been reported with installation of baffles inside the drum and layout at a certain angle to avoid ash accumulation and agglomeration. Rotary kilns have a lower heat transfer rate due to movement at a particular speed and the drawback of inefficient sealing is involved. While plasma reactors are promising for wet sewage sludge and removal of pollutant gases at higher temperatures, however they require high input energy which is difficult to justify at commercial scale.

Moreover, many factors are dependent on the selection of the reactor technology to be used for the gasification of sewage sludge. These factors are temperature, pressure, nature of feed stock, moisture content, particle feed size, feed rate, equivalence ratio of air/sewage sludge, steam to sewage sludge ratio. In addition, if a catalyst is being added for tar and syngas reforming then proper selection of the catalyst is needed, its position within the reactor system (in-situ or ex-situ) and its effects on the desired product should be known. Each reactor technology has varying results with respect to these factors or operating conditions. Using one reactor in which gasification with the help of steam and catalyst are all in one place can be advantageous to save time and cost. This kind of configuration is highly recommended. Fock et al. [208] have investigated a vortex flow gasifier to decrease the tar content from syngas. The design of a vortex flow gasifier consists of one stage reactor feeding air and fuel from the top. The air flow is made to rotate horizontally going downwards and with a secondary flow in an upward direction in the middle of the gasifier. This design was basically to make the pyrolysis and char combustion in one downdraft gasifier in which combustion of volatiles takes place in the upward direction due to supply of air. Experiments were carried out for wood chips at 100kW capacity, however, there was less further detail reported. In an another study for coal gasification, Elliot et al.[209] made changes to the vortex gasifier as input of air at various inlets, but further evidence of gasification reactions, char and ash controls and other operating conditions were not provided. Thus, these vortex flow gasifiers may have potential for sewage sludge gasification as single stage reactors, but more in depth studies are required.

5.2.1 Technological Strength and Market Competitiveness of Gasification Reactors

Based on the properties of gasification reactors, technological strength and their market competitiveness can be evaluated. The properties of gasification reactors can be converted to scale values using the Analytical Hierarchy Process (AHP), similar to pyrolysis reactors (Section 4.3.1).

Table 15 and Fig. 20 shows the scale values for technological strength and graphical representation of market competitiveness of gasification reactors. The auger reactor is deemed as more attractive towards market viability according to this analysis. The tar reduction attribute is shown as positive and ash agglomeration is illustrated as negative. Plasma reactors have shown more complexity requiring a high input energy prerequisite. Reactors with more ash agglomeration have less technological strength and market competitiveness for sewage sludge. A number of problems add complexity and in turn more cost for gasification of sewage sludge.

Table 15: Technological strength of sewage sludge gasification reactors.

Reactors	Syn gas	Tar reduction	Feed size	Inert gas	Scale up	Complexity	Heat transfer	Ash Agglomeration	T.S
BFBR	10	10	3	3	10	3	10	3	52
CFBR	10	10	1	3	10	3	10	3	50
Auger	6	6	6	10	10	10	10	6	64
Rotary	6	6	6	10	10	10	3	6	57
Plasma	10	10	6	6	10	1	10	3	56

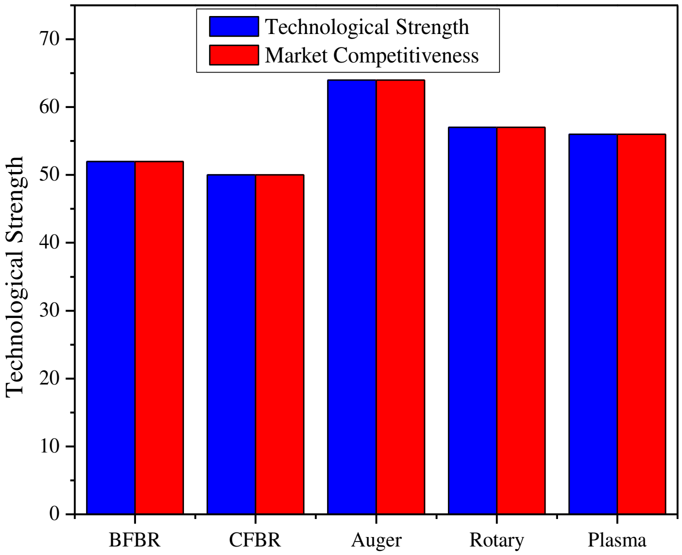


Fig. 20: Technological strength and market competitiveness of sewage sludge gasification reactors.

5.3 Operating Parameters for Gasification of Sewage Sludge

5.3.1 Moisture Content, Feed Size and Feed Rate

A dried sewage sludge is required for the production of good quality syngas in gasification otherwise torrefied, pyro char or hydro char having less moisture may be required for utilization. Plasma gasifiers have potential to treat the wet sewage sludge and produce syngas with reduction in pollutants. A wise selection of drying technology and other optimal conditions are indispensable for the optimal quality and quantity of the syngas. To obtain a high yield of product gas, the feed particle size and the rate at which the feed is being fed to the reactor, play an important role. Sensitivity towards the particle sizes are in order of increasing particle size, circulating fluidized bed reactor>bubbling fluidized bed reactor>fixed bed reactor. An efficient heat transfer rate leads to improved gasification reactions resulting in high H_2 and CO values and reduced tar content. A low flow rate of feedstock and higher gas residence time would lead to higher char conversion and more transformation of carbon content to the gaseous state. However, at lower gas residence time and high feed flow rate, the reactions would not be completed and the desired product losses its quality. Optimized feed flow rate and gas residence time are favorable.

5.3.2 Equivalence Ratio

An equivalence ratio (ER) is the actual air to sewage sludge mass ratio used in gasification with respect to the air to sewage sludge mass ratio required for stoichiometric combustion. ER has a key impact factor on the gasification of sewage sludge. Many researchers have found that at lower ER, hydrogen and carbon monoxide content is higher, but at a low ER the gas products would also decrease, similar to the start of pyrolysis. On the contrary, low hydrogen and carbon monoxide and higher carbon dioxide content would be produced at higher ER resulting in low heat content of the syngas. It has also been found that due to higher ER, more oxygen reacts with volatiles and results in enhanced tar cracking. Too lower or higher ER may lead to difficulties in the gasification of sewage sludge. Hence, 0.2 to 0.35 is the range of equivalence ratio to obtain good results [210-212].

5.3.3 Steam/Sewage Sludge Ratio

Steam to sewage sludge ratio (S/SS) is the amount of steam being injected with sewage sludge into the reactor. The reactions involving steam have vital importance in steam gasification and hydrogen production. Studies have shown that syngas production of higher heating value can be generated with lower tar and char content by using steam rather than air gasification. The S/SS ratio is a significant factor in steam gasification because the steam reforming reaction is the key reaction to produce H_2 [213]. At lower ratio of S/SS, the syngas may have elevated contents of char, tar and methane. The elevation of S/SS ratio from 0 to 2 gives improved impact on H_2 content, char gasification, tar reforming and dry gas quality. Researchers have found that the generation of hydrogen and carbon monoxide during the gasification reaction completely relied on the quantity of steam, whereas the CO_2 and CH_4 are controlled by the temperature of reactor [214]. Therefore, the optimal S/SS of 0 to 2 has importance in sewage sludge gasification along with other operating conditions.

5.3.4 Temperature & Pressure

A major controlling process parameter for the gasification of sewage sludge is the temperature, which influences the completion of gasification reactions, combustion, Boudouard reaction, water gas shift reaction, methane formation and steam methane reforming reactions. Methane decomposition involves hydrocarbon reformation reactions. While hydrogen yield rises largely because of the methane decomposition, steam reforming, and hydrocarbon reforming reactions. Higher temperature has very good impacts by giving higher yields of syngas and reducing the tar and char yields. An abundant amount of char would be converted into gaseous content with high temperature. High temperatures help in producing higher carbon dioxide and lowering the heating value of the produced gas. Temperatures greater than 800°C would lead to high conversion of carbon and high molecular weight hydrocarbons to form gas and consequently cold gas efficiency would be increased [191]. The cold gasification efficiency is the ratio between the energy contained in the product gas and the energy contained in the mass of sewage sludge fed. Nevertheless, too higher temperature may lead to clinker formation due to the high ash content of sewage sludge. The partial pressure of the gasifying agent in the reactor is of critical importance which has impact on the desired product yield. An optimum partial pressure is needed to have more interaction with components present in the reactor along with an optimum temperature which is responsible for the heating rate to convert sewage sludge into high quality syngas.

5.3.5 Catalyst Addition

The purpose of catalyst addition in the gasification system is to promote the gasification process and to degrade the tar contaminants to produce higher yield of syngas. Tar is a complex mixture of higher hydrocarbons which needs to be cracked down to lower molecular weight hydrocarbons in the gas phase to obtain more hydrogen, carbon monoxide and methane. The catalyst enables heat and mass transfer between particles in a befitting manner. Some catalysts are added to the reactor as an additive or substitute for the sand. As the important reactions in gasification that play a vital part are all endothermic, catalysts are used to lower the activation energy to produce high yields of product gas and to improve the gasification efficiency. The placement of catalyst in the reactor is dependent on the reaction carried out.

5.4 Co-gasification of Sewage Sludge

In the gasification process, the properties of sewage sludge affect the produced products and during the process the intrinsic properties have an impact on lowering the quality of the desired product. Use of pyrolysis char and sewage sludge is common in laboratory scale experiments and also in commercial small to medium gasification plants. Table 16 shows the gasification results from sewage sludge and pyrolysis char. Gas yield, tar content, CGE, LHV and pollutants like NH_3, HCl and H_2S may vary depending upon the reactors and other conditions. The pollutants containing NO and N_2O gases, convert into NH_3, HCN and further reduce to N_2 because of the presence of Fe_2O_3 and CaO in chars during sewage sludge gasification. During sewage sludge gasification, 271 mg/Nm^3 and 592 mg/Nm^3 of NH_3 and HCN in syngas and, 1.4 (wt.%) and 0.5 (wt.%) of nitrogen and sulfur in residues have been reported [200]. Higher nitrogen and sulfur content in sewage sludge need to be minimized in order to avoid NOx and SOx during gasification. To clean the syngas and remove such kinds of pollutants, the use of scrubbers, use of other feedstocks and catalysts may be used. Gasification of pyrolysis char may give good results rather than using sewage sludge directly, because of the more active pores sites in the char for the gasification reactions in the presence of steam or air. However, the factor of ash content and heavy metals concentrated in chars cannot be ignored.

In order to increase the product quality and to reduce the pollutants, ash and heavy metal content, co-gasification of sewage sludge with coal and biomass: torrified biomass [215], woody biomass, saw dust, forestry waste is common using air and steam. In small to medium pilot scale plants co-gasification of sewage sludge is also being used. CGE for co-gasification with wood pellets and paper sludge is reported as 59.3% and 61.6%, more than sewage sludge at 55.12%. Total dry gas yield is higher for co-gasification with coal (2.5-2.7 Nm^3/kg). Addition of sewage sludge with coal can decrease the CO_2 emissions which are higher in the case of only coal being used. The information on release of pollutants in the dry gas product during co-gasification of sewage sludge is less reported, however it can be anticipated that H_2S and NH_3 values are higher as compared to HCl, HF and PAHs due to higher sulfur and nitrogen content in sewage sludge. In addition, it can be concluded that, more mineral CaO and Fe_2O_3 content may have reduced these pollutants. Moreover, co-gasification of sewage sludge gives potential to reduce the residual ash and to decrease the level of pollutants. Co-gasification with biomass can produce a reduction in NH_3 and H_2S. During co-gasification, the gas yields may become lower, however, it is favorable to produce products with high energy content and high carbon conversion. Low tar content, better yield of syngas, LHV and cold gas efficiency are required to add the biomass or coal with sewage sludge as illustrated in Table 17.

Table 16: Gasification results of sewage sludge and char [216-219].

	Sewage sludge	**Pyrolysis char**
Carbon fraction in solid (wt.%)	9.01	30.13
Gas yield (m^3/kg daf)	1.12	1.23
Tar (wt.%)	5.28	2.94
H_2/CO (molar ratio)	2.21	1.48
CO/CO_2 (molar ratio)	0.52	0.85
Gas composition (g/kg daf)		
H_2	37.03	32.80
CO	250.10	427.16
CO_2	763.42	815.96
CH_4	50.23	10.33
C_2H_x	46.13	0.28
H_2S	12.66	3.54
LHV (MJ/m^3)	5.49	5.09
CGE (%)	55.12	52.22
Carbon yield to gas phase (wt.%)	72.48	64.29
Energy recovery efficiency (%)		0.99

Table 17: Product yields of co-gasification of sewage sludge.

	SS/WP [211]	**SS/PS** [220]	**SS/WP** [221]	**SS/FW** [222]	**SS/C** [223]	**SS/SD** [224]
Gas yield (Nm^3/kg)^a	1.32	n. r	1.72	0.62	2.51-2.7	0.99
Tar (wt.%)	n. r	n. r	n. r	16.1	1.6-3.5	n. r
Gas composition (vol.%)^a						
H_2	4.5	4.13	4.61	35.1	8.10	6.5
CO	18.5	4.70	17.10	29.3	9.24	20.3
CO_2	14.9	22.37	14.3	21.4	n. r	70.5
CH_4	1.93	3.65	2.45	7.3	1.54	5.6
C_nH_m	4.42	1.24	4.8	6.9	0.49	
LHV (MJ/Nm^3)	5.38	2.42	5.41	12.17	2.88	5.88
CGE (%)	59.3	61.6	52.3	n. r	n. r	41.39
CCE(%)	n. r	n. r	n. r	68.55	n. r	n. r

a= dry ash free base, n. r= not reported, WP=wood pellets, PS= paper sludge, FW= forestry waste, C=coal.

The ash collected from electrostatic precipitators, cyclones and fabric filters during gas cleaning contains heavy metals and is a major problem to treat. Due to high ash content, dry gas yield and cold gas efficiency are affected leading to more tar which is a major constraint in gasification reactions and the downstream further use of syngas. In Table 18, the mineral content and heavy metal content are shown from co-gasification of sewage sludge with coal, saw dust and woody biomass. Mineral content for example Na_2O, MgO, Fe_2O_3, TiO_2, Al_2O_3, SiO_2 and CaO are promising for further catalytic use even during gasification. These minerals can also add value in cement manufacturing, adsorbents, ceramics and agriculture. High concentrations of heavy metals like Zn, Cd, Cr, Ni, Si and Al can restrict the use of gasification ash in agriculture and land applications. The recovery of P (73-82%) and K elements from gasification ash by using mineral acids is interesting for fertilizer use [225]. High concentration of P_2O_5 and K_2O in ash has been observed for sewage sludge rather than blends with other feedstocks. Hence, the origin of the feedstocks also significantly matters for gasification and co-gasification. To cope with ash and tar content, and to increase the energy level of products, different kinds of catalysts can be used in gasification and co-gasification of sewage sludge.

Table 18: Minerals and heavy metals in ash after co-gasification of sewage sludge.

Minerals (wt.%)[a]	**SS [226]**	**SS [200]**	**SS/C [227]**	**HM**	**SS (wt.%)[a] [218, 227]**	**SS/C (wt.%)[a] [227, 228]**	**SS/C (wt.%)[a] [229]**	**SS/SD (wt.%)[a] [224]**	**SS/SW (mg/kg)[a] [206]**	**SS/WB (mg/kg)[a] [221]**
Na_2O	0.15	0.56	0.41	Fe	0.99	26.77	n. r	3.17	31, 852	n. r
MgO	1.60	5.84	6.80	Ti	0.92	0.60	n. r	0.97	1305	n. r
Al_2O_3	3.31	9.46	10.09	Ca	17.55	26.45	49	1.30	62, 769	n. r
SiO_2	12.09	25.48	28.36	K	2.92	1.57	40	1.09	9448	n. r
P_2O_5	9.05	28.77	8.12	P	11.22	6.03	n. r	n. r	37,743	n. r
K_2O	0.55	4.63	1.11	Si	1.48	22.36	n. r	1.04	70, 953	n. r
CaO	3.85	10.75	21.88	Al	11.93	8.84	n. r	2.14	13,358	n. r
TiO_2	0.43	0.81	0.60	Mg	0.84	6.86	60	0.90	10, 939	n. r
Fe_2O_3	9.28	10.84	22.63	Na	0.01	0.53	58	0.43	1883	n. r
				Cd	n. r	0.20	18	n. r	n. r	0.4
				Cr	n. r	0.30	48	n. r	157.9	135
				Ni	0.04	0.23	87	0.02	9.35	66
				S	n. r	n. r	20	n. r	n. r	n. r
				Cu	0.01	0.19	n. r	0.14	148.2	834
				Zn	0.19	0.09	n. r	0.05	909.2	1342

a= dry basis, SS= sewage sludge, C= coal, SD= saw dust, WB= woody biomass, SW= softwood, n. r= not reported.

5.5 Catalytic Reforming During Gasification

5.5.1 Syngas & Tar Reforming

Syngas is mainly composed of H_2 and CO, with also CO_2, CH_4 and C_2-C_3 gases present. Hydrogen is considered as one of the cleanest energy carriers which can be produced from renewable energy resources for carbon dioxide emission reduction as a solution to environmental problems. Along with H_2 and CO, CO_2 and CH_4 and other contaminants are produced in the gasification of sewage sludge for example, H_2S, HCl, NH_3 and tar which are problematic. It is well known that the fuel to be used in internal combustion engines should have light hydrocarbons to combust easily and efficiently, so the cracking or reforming of tar is essential for the syngas produced from sewage sludge to be used in gas engines. The role of the catalyst is not only reforming tar but also to produce higher yields of H_2 and CO having high energy level with reduction in NOx and SOx. Tar compounds found during gasification of sewage sludge are (1) N-aromatics (50%): methyl-pyridine, benzo-nitrile, quinoline, indole, phenyl-pyridine, benzoquinoline and pyridine. (2) O-aromatics (2.6%): phenol and benzo furan. (3) S-compounds (4.9%): 2-benzothiophene and propane nitrile. (4) Light Aromatics (6.5%) and PAHs (36%): indene, naphthalene, methyl naphthalene, biphenyl, biphenylene, fluorine, anthracene and phenanthrene [216, 230, 231]. Tar reforming involves different reactions such as catalytic reforming and thermal reforming. The advantage of catalytic cracking is the reduction in activation energy at lower temperature to decompose the tar. The catalysts investigated in the literature for tar and syngas reforming in sewage sludge gasification are: Ni and Fe based catalysts, alumina, silica sand, TiO_2, dolomite, olivine, CaO, natural zeolite, bio-char and activated carbon. The effect of these catalysts is represented in Table 19 for improvement in syngas yields, LHV, CGE and reduction in tar and pollutants.

(a) Bio-char and Activated Carbon

Bio-char produced from pyrolysis and gasification has the potential to be used as a catalyst. As bio-char produced from the gasification process is lower in quantity than pyrolysis, its surface area and carbonaceous content make it one of the superior bio-chars for catalyst use produced from wastes and biomass. The reason is having metal (Na, K, Ca, P, Mg and Al) and mineral contents (MgO, Fe_2O_3, Al_2O_3 etc.), resulting in improved catalytic activity. Usually, bio-chars are activated by steam and chemicals to enhance the surface area and active pores size. In gasification most of the reactions involve steam and water which make them more promising catalysts. Bio-char from woody biomass have higher surface area than grass residues and almost 80% carbon content. Sewage sludge too has high surface area (500 m^2/g) and carbon content (90%) [232]. Therefore, co-gasification of sewage sludge char with woody biomass is effective. Moreover, dispersion of metals (Ni, Fe, Co, Mo, Ce) on bio-char can further enhance the catalytic activity for tar reforming and reduction of pollutants. Recently, most researchers have also used coal based activated carbon and found excellent results for syngas with added LHV, gas yield, overall gasification efficiency, tar removal and eradication of toxic gases. The ash from gasification of sewage sludge has sufficient mineral content, which can be more effective than Al_2O_3, SiO_2, TiO_2, ZrO_2, CeO_2 and zeolites for utilization as support material for the catalyst. It is anticipated that less sintering and deviation in structure would be observed at higher temperatures by using sewage sludge ash. Hence, the gasification products bio-char and ash have not only positive environmental impact but can also contribute to process economics.

(b) Nickel Based Catalysts

Ni is known to be effective for the cleavage of C-C, C-H and C-O bonds in reforming and tar cracking reactions. Few researchers have reported Ni impregnated on activated carbons, lignite char and bio-chars to enhance the catalytic activity for tar and syngas reforming. The dispersion of nano-particles of Ni gives higher surface area if it is impregnated on lignite char. The size of nano-particles grows bigger on increasing the temperature during the carbonization, in turn it gives more catalytic activity due to wider crystallite size as shown in Fig. 21. However, at higher temperatures there is more chance of coke deposition by using Ni. NiO impregnation on alumina, activated carbon and bio-chars gives promising results for higher syngas yields with improved LHV. NiO on ceramic foam due to higher pore activity and stability is encouraging for higher yields and LHV of gases. Noble metals are recognized for enhanced catalytic activity, nonetheless they are expensive, however, Ni, Co, Mo are inexpensive metals and can contribute well for gasification of sewage sludge. Ni-based activated carbons and bio-chars are effective for removal of N-containing compounds in tars and reducing NH_3 in gases. Use of La_2O_3, perovskites, hydrotalcite, and zeolites have produced good results for catalytic activity and stability. The formation and preparation methods are complex which makes them (La_2O_3, perovskites, hydrotalcite, and zeolites) less suitable for sewage sludge, if the desired purpose is not being fulfilled with natural catalyst, catalyst with easy preparation and easy regeneration, then these can be tried in sewage sludge gasification for reforming and reducing pollutants.

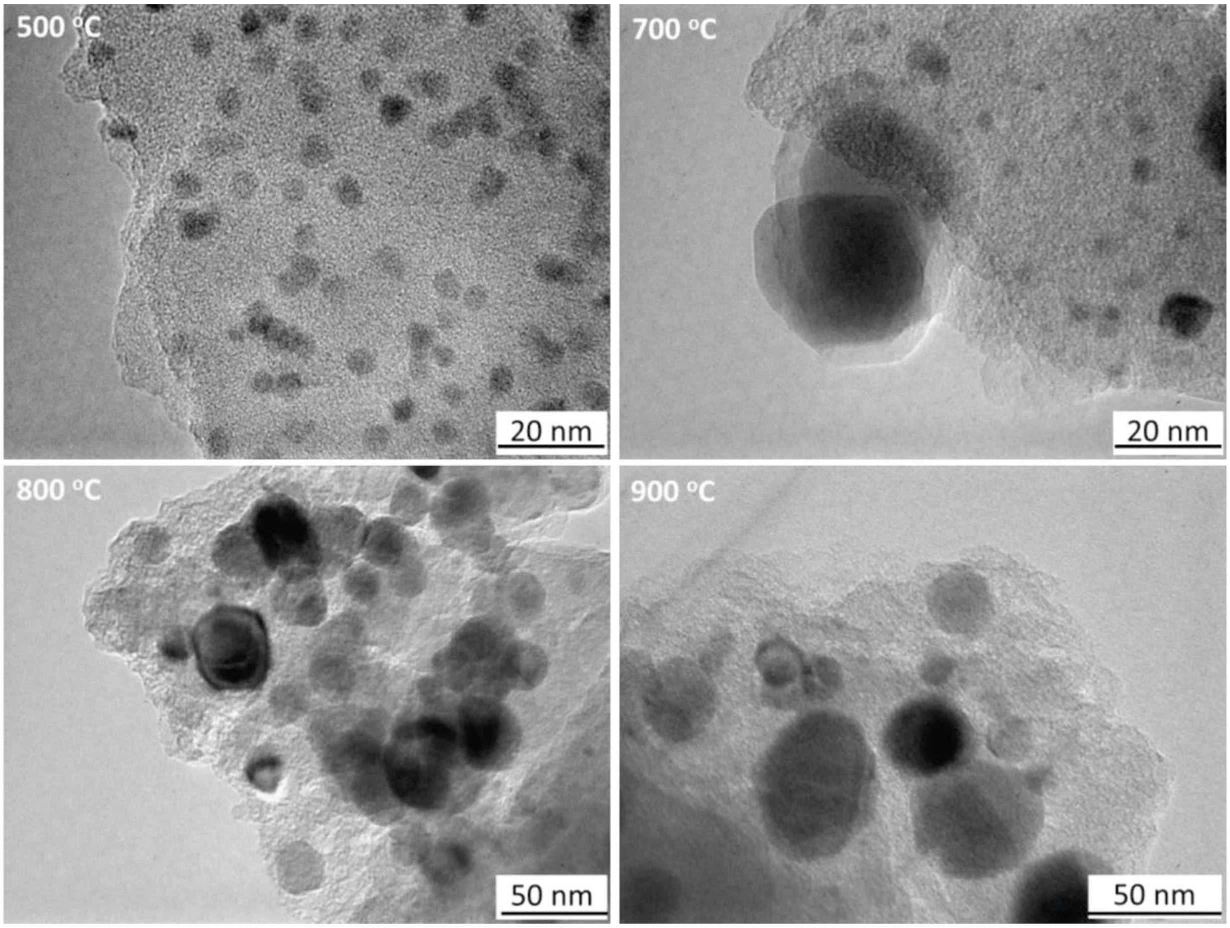


Fig. 21: TEM images of Ni impregnated on lignite char [233].

(c) Dolomite, Olivine and their Effects

Many studies have reported the use of dolomite Ca-Mg$(CO_3)_2$ and olivine (Mg-Fe)$_2SiO_4$ as effective additives to obtain higher hydrogen gas yield. Olivine has more resistance towards attrition than dolomite and it shows a slightly lower activity in sewage sludge gasification for tar removal having the same gas yields and LHV. Olivine and dolomite in combination with activated carbons, bio-chars or metals like Ni, Fe, Co, Mo can provide favorable results. Dolomite is reported to be used as an additive due to its appropriate resistance towards catalyst deactivation and coke deposition. Dolomite with steam is effective to reduce the tar content especially benzene and PAHs from 30 to 10 mg/g sludge daf and 0.27 to 0.18 mg/g sludge daf respectively [231]. A comprehensive comparison can be conducted for sewage sludge gasification with dolomite, olivine, biomass activated carbon, coal based activated carbon and zeolites. The highest gas yields and tar removal efficiencies with combination of coal based activated carbon and dolomite is interesting to observe. The catalytic activities and spent activities are important to know for making any comprehension about the efficiency of catalyst. Fig. 22 shows the total tar content and tar removal efficiency by different catalyst combinations. The spent activity of coal based activated carbon and dolomite have also shown higher tar removal than other additives and combinations. Whereas activated carbons are non-polar and sewage sludge contains more N-compounds which are polar in nature. So, used alone activated carbons cannot decrease the tar content whereas addition of additives such as olivine and dolomite can increase the tar removal efficiency.

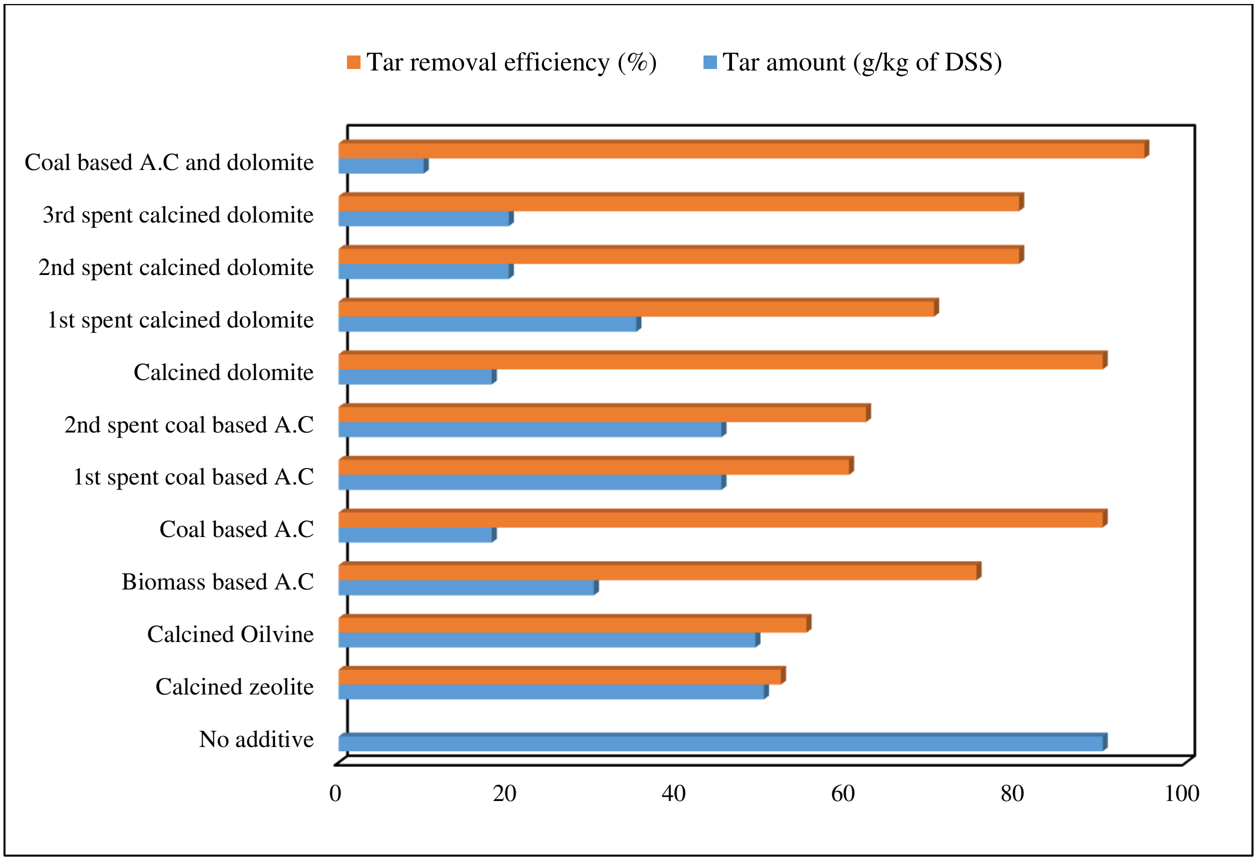


Fig. 22: Tar removal efficiency with different additives [230].

(d) CaO and its Effects

Calcium oxide (lime) has wide importance in producing more hydrogen and capturing carbon dioxide. Besides, producing high hydrogen yield it has an effective impact on reducing tar, N and S compounds. Calcium oxide has applications in sewage sludge gasification as both a conditioner and additive, but is more effective as a conditioner rather than as an additive. As conditioner CaO is converted into $Ca(OH)_2$, and performs the catalytic action while as an additive CaO remains the same. Ca species are considered to break the C-C and C-H bonds to crack the large molecules into lower molecular weight species. The combination of Fenton's reagent and lime gave promising results in reducing NOx and SOx. As sewage sludge has more nitrogen content in the form of N-pyrroles, N-pyridine and N-nitriles, Fenton's reagent converts nitriles and pyrroles into amine and pyridine and further into indole in tar. The indole is stable and difficult to decompose, in-turn reduction in HCN and NH_3. Iron salts are also favorable for sulfur reduction during sewage sludge gasification. Calcium salts convert Quaternary-N into amines and pyridines and further into N_2. Fe and Ca salts react with proteins and amines of sewage sludge and form Fe-N and CaCx-N and further decompose to give N_2 as in Eq. 2, 3 and 4 [234]. Similarly, CaO reacts with H_2S to eradicate sulfur as sorbent Eq. 5 [235].

$$\textbf{Fe-N} \rightarrow \textbf{Fe} + \textbf{N}_2 \qquad \textbf{Eq. (2)}$$

$$\textbf{CaCx-N} \rightarrow \textbf{CaCx} + \textbf{N}_2 \qquad \textbf{Eq. (3)}$$

$$\textbf{Fe-N} + \textbf{CaCx-N} \rightarrow \textbf{Fe} + \textbf{CaCx} + \textbf{N}_2 \qquad \textbf{Eq. (4)}$$

$$\textbf{CaO} + \textbf{H}_2\textbf{S} \leftrightarrow \textbf{CaS} + \textbf{H}_2\textbf{O} \qquad \textbf{Eq. (5)}$$

In addition, CaO with support materials Al_2O_3, TiO_2, SiO_2 and dispersion of metals like Ni, Co, Mo, and Ce has great potential for more hydrogen production and tar removal. The only problem is its deactivation during regeneration which presents discontinuous hydrogen production. A concept has been proposed for CaO based chemical looping. Because of the energy efficient and economic aspects, the calcium based looping gasification has gained more attention in recent years. A schematic diagram of chemical looping is shown in Fig. 23. Essentially, the lime absorbs carbon dioxide via an exothermic carbonation reaction and by endothermic calcination it releases its captured CO_2 reversibly, which can be used for dry reforming as presented in Eq. 6 [236, 237]:

$$\textbf{Carbonation: } \textbf{CaO}_{(s)} + \textbf{CO}_2 \leftrightarrow \textbf{CaCO}_{3\,(s)} \qquad \Delta \textbf{H}_{298} = \textbf{-178.2 kJ/mol} \qquad \textbf{Eq. (6)}$$

This exothermic reaction provides heat to other reactions of gasification and leads to more hydrogen production and tar reforming. Use of lime for the capture of CO_2 and tar cracking has the benefit of being an exothermic reaction. Moreover, it also has also the benefit of increasing heat rates for enhanced CGE and influencing water gas shift equilibrium for hydrogen production at lower temperature.

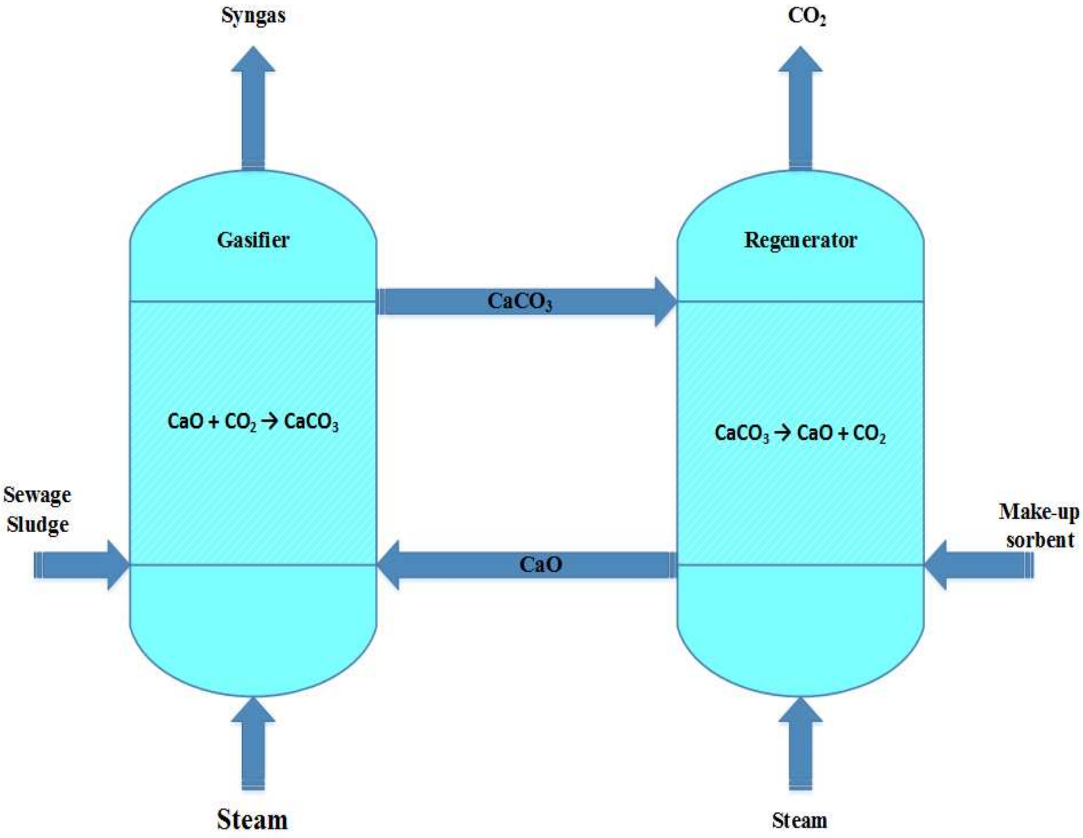


Fig. 23: Schematic diagram of calcium based looping gasification.

Table 19: Effect of catalysts and conditioners on gasification and co-gasification of sewage sludge.

Feed Type	Reactor System	Temp.	Catalyst & operating conditions	Observation	Ref
DSS	Auger, fluidized bed, and fixed bed	650, 810 & 830°C	A.C, ER: 0.22-0.50, Air: 9-14L/min, A.C/SS:0.5-2.	Highest H_2 content in producer gas (29 vol.%) was obtained at the A.C/fuel ratio of 3:1 and at an equivalence ratio of 0.35. Tar:27 mg/Nm^3, NH_3:443ppm, H_2S:470 ppm were found at minimum level. Highest CGE and CCE: 97.69 and 91.18% were reported.	[210]
DSS	Bubbling fluidized bed reactor, fixed bed reactor	800 °C	Natural Zeolite, Olivine, coal based A.C and dolomite, time:47-50 min, ER: 0.17-0.20, air injected.	Highest H_2 (28 vol.%) and CO (21 vol.%) yields were with coal based A.C rather than other catalysts. Maximum reduction in tar in syngas was also found with coal based activated carbon: 0.17g/Nm^3, total tar: 8.44g/kg DSS. Dolomite also shown results near to A.C.	[230]
DSS	Fluidized bed reactor and fixed bed reactor	780-810 °C	A.C, Ni-A.C, dolomite, CaO, time:75-220 min, ER:0.35-0.36, Air: 13Nl/min, Feed rate: 10.7-10.9g/min.	A Ni-impregnated A.C gave higher H_2 (31vol.%) and tar free syngas. Tar removal efficiency:97% and 114 ppm of NH_3 lowest of all catalysts. Overall NH_3 with other catalysts was 146 ppm.	[238]
DSS	Laboratory scale bubbling fluidized bed reactor	750-850 °C	Alumina: 0,10 and 15%, ER:0.2-0.4, S/SS:0-1, 80g of Silica in each test, time:50 min.	CGE and CCE are 10% and 5% higher than non-catalytic process. Steam and alumina gave 46% more H_2 with higher LHV of 3.7MJ/Nm^3 as compared to non-catalytic gasification.	[239]
DSS	Auger, fluidized bed and fixed bed reactor.	640-820 °C	Ni and Fe based A.C, Time:61-220, Air:17Nl/min, ER:0.3.	Ni/A.C produced highest H_2 (28 vol.%) and NH_3 198 ppm with highest tar removal efficiency 91%. While Fe/A.C produced less H_2S content of 96 ppm with tar removal efficiency 92% and H_2 26 vol.%.	[22]
DSS	Fluidized bed reactor and fixed bed reactor	790-806 °C	Calcined dolomite and A.C, time:47-90 min, ER: 0.19, Air: 10 and 15NL/min.	Calcined dolomite with DSS was in fluidized bed reactor, A.C has been used for tar removal. The total tar removal efficiency and the H_2 content in syngas were 88.4% and 32.1 vol.%. LHV of syngas was 7MJ/Nm^3.	[240]
RSS	Fixed bed reactor	873,1073,1273K	Fenton reagent and CaO.	The combination of Fenton's reagent and CaO can complementarily reduce the HCN and NH_3 13.71-17.67 mL/g and 17.77-23.45 mL/g. These are also proved to decrease the tar content.	[234]

DSS	Laboratory scale fluidized bed reactor	750, 800, 850 °C	Olivine, alumina and dolomite ER:0.3,air+steam/SS=1.	Dolomite showed 45% reduction in tar content and 90% decrease in PAHs as compared to alumina (35%) and olivine (20%). It was observed that hydrogen and carbon dioxide content elevated and les tar produced by combination of air and steam with catalyst.	[241]
DSS	Laboratory scale fluidized bed reactor	800 °C	Dolomite, ER:0.3, air + steam, S/B:0-1	H_2 gas was increased up-to 20-36% with tar removal efficiency 71%. Highest LHV of gas and CGE were 3.6MJ/Nm^3 and 50%. Highest gas production was 3Nm^3/kg of DSS.	[231]
DSS	Fixed bed reactor	650-850 °C	Ni-Fe based CaO, CaO-TiO_2, CaO-Al_2O_3 and CaO-3A, Time: 1 hr.	H_2 production was increased from 72-82% at 650°C. Highest surface area was for 3A molecular sieves which leads to more CGE (78%) as compared to others. Addition of metal element Ni and Fe enhanced the tar cracking, methane reforming and char conversion into gases.	[242]
WSS and PSD	Fluidized bed and fixed bed reactor	600-900°C	NiO/modified dolomite, N_2: 0.37m/s.	Tar yield: 2.19%, dry gas yield:1.23 Nm^3/kg, LHV of gas:10.65MJ/Nm^3, CCE:85%. Optimal blend ratio is 40/60 PSD and WSS.	[243]
DSS	Lab scale fixed bed reactor	600°C	$Ca(OH)_2$ and $Ni(OH)_2$, heating rate 50°C, distilled water 0.3g/min.	Hydrogen yield (93%) was almost 70g/kg of DSS. High yield of hydrogen is due to hydroxides and their catalytic effect.	[244]
DSS	Lab scale fixed bed reactor	873K, 1073 K and 1273K	Fenton peroxide and CaO, DSS 0.2g/min, S/B:1.6, Ar:700Nml/min.	Hydrogen yield 200Nml/g, CCE:97% and CGE 78% at 1273K, H_2S: 0.19% and NH_3:0.01% at 1273K.	[245]
DSS	Lab scale two-stage fixed bed reactor	500-750 and 900°C	Ni/lignite char and Ni/Al_2O_3, steam 30kpa and 120ml/min.	N-char, NH_3, HCN, N_2 and N-tar are 20%, 40%, 2%, 20% and 10% for Ni/lignite char at 650°C. N-char, N_2 and N-tar are 20%, 75% and 5% for Ni/Al_2O_3 at 650°C. 55mmol/g daf of H_2 yield with steam and Ni/lignite char.	[233]
DSS	Lab scale bubbling fluidized bed reactor and fixed bed reactor	800°C	Acid treated A.C, A.C and CaO. ER:0.25, preheated O_2:7NL/min	H_2:52.2vol.%, tar removal efficiency 92-96%, CGE:90%. Acid treated A.C showed less efficiency in tar removal rather that A.C. NH_3 20ppm was found with A.C	[246]
DSS	Lab scale fixed bed reactor	873, 973 and 1073K	CaO, S/C:1.6, water: 0.2g/min, nitrogen: 0.6NL/min	H_2:282Nml/g, LHV of gas:18MJ/Nm^3 at 1073, and CGE 1.9kJ of gas/kJ of solid.	[236]

DSS	Lab scale bubbling fluidized bed reactor and fixed bed reactor	763-812°C	Olivine and coal based A.C, ER:0.20-0.22, S/C: 1.11. Ni-coated distributor. air:10NL/min.	H_2:34vol.% and tar removal efficiency was 98%. NH_3:11ppm.	[247]
Acid hydrolysis residues and sewage sludge	Lab scale fixed bed reactor	600-800°C	CaO, nitrogen:1L/min, ER:0.15-0.30.	LHV, gas yield, CGE and tar yield at 800°C were 5.68MJ/Nm^3, 1.26Nm_3/kg, 65% and 4.42 g/Nm^3.	[248]
DSS and coal	Two zone reactor system, bubbling fluidized bed reactor and fixed bed reactor	850°C	Dolomite and Ni/alumina, air flow rate:2.81 dm3/min, feed rate: 2.3g/min, initial sand bed 300g.	H_2:7.9vol.%, LHV of gas: 2.6MJ/m^3, tar:2mg/m^3, H_2S removal 1100-300 ppm.	[249]
DSS and coal	Bubbling fluidized bed reactor and fixed bed reactor	800°C	Fe/coal based A.C, air preheated at 450C, ER:0.3, feed rate 13g/min.	H_2:30v.ol%, LHV 5MJ/Nm^3, tar: <0.1, CGE: 85%, CCE: 66%, NH_3 392 and H2S 229 ppm.	[250]

5.5.2 Syngas in Combined Heat & Power (CHP) and Biofuel

Syngas produced from the gasifier has the potential to be used in combined heat and power plants. The gasification process gives a significant amount of energy in the form of syngas that can be utilized to obtain energy. Data has been collected for pilot, demonstration units and commercial scale plants which are using sewage sludge as a feedstock to produce heat and power and is depicted in Table 20. This gathered data shows that syngas from sewage sludge can play a vital role in internal combustion engines and small to medium boilers having an average energy value of 5.5 MJ/Nm^3 for LHV. A very few number of plants are reported which are using sewage sludge with other feedstocks like biomass for co-gasification. The heat and power produced from sewage sludge gasification plants is being used for electricity consumption of their own plants, fulfilling their requirement for drying operations and producing electricity for commercial purposes. Syngas produced either from sewage sludge or from co-gasification with coal and biomass is also commendable to produce heat and power. However, co-gasification and catalytic gasification may add more energy content to the syngas in terms of CCE, CGE and LHV. Not only to produce heat and power, the syngas is useful to produce liquid fuels and chemicals by the Fischer-Tropsch synthesis process. By using the Fischer-Tropsch process, fuels and chemicals like methanol, ethanol, gasoline, di-methyl ether can be produced by further catalytic reactions and distillation at high temperature and pressure. A comprehensive flow diagram of sewage sludge gasification is shown in Fig. 24. Thus, sewage sludge being a waste material can contribute to add value in energy and power, to lessen the burden from fossil fuels and to decrease GHG emissions.

In the context of the circular economy and the wide range of products and by-products produced from gasification of sewage sludge seems appropriate and feasible. The energy recovery from syngas, use of char and ash for catalyst or adsorbent and recovery of P, N, and K are all value addition for the circular economy. Hydrogen separation from syngas to produce a renewable fuel is most interesting for researchers. The viability of sewage sludge gasification depends on many factors which includes quantity of raw sewage sludge production, capital costs for installation of plants, operation and maintenance costs, technology to be used, electric or thermal power for drying operations, quality of products and by-products, land cost, labor cost and other utility costs. These costs vary for every different scenario and location or region. So, it is difficult to give the exact statistics for the profit generation and energy recovery from the gasification process. However, using sewage sludge for gasification, the nature and quality of products, by-products and toxicities associated with them are obvious. The control measures should be in place to avoid pollutants. Toxicity of sewage sludge is contained in gas (NOx, SOx, HF, HCl, PAHs and dioxins, liquid-tar (N, O and S compounds) and solid (heavy metals).

Table 20: Pilot and commercial scale sewage sludge gasification plants.

Reactor	Location	Type	Details	Ref.
Low temperature-circulating fluidized bed reactor (LT-CFBR)	Technical University of Denmark	Pilot scale	Capacity: 100kW$_{th}$ Co-gasification of SS and CS	[202, 229]
LT-CFBR	Kalundborg, Denmark	Commercial scale	Capacity: 6MW$_{th}$ Co-gasification of SS and CS	[202, 229]
Fluidized bed reactor	University of Seville, Spain	Pilot scale	Capacity: 100kWth Gasification of SS	[201]
Bubbling fluidized bed reactor	Balingen, Germany	Demonstration Unit	Capacity: 720kW Power to CHP: 75 kW CGE:66% Gasification of SS	[251]
Bubbling fluidized bed reactor	Mannheim, Germany	Demonstration Unit	Capacity: 2.2MW$_{th}$ Power to CHP: 75 kW CGE:70% Gasification of SS	[251]
Bubbling fluidized bed reactor	Tao-Yuan, Taiwan	Commercial scale	Capacity: 3MW$_{th}$ Co-gasification of SS and PMS	[220]
Fixed bed reactor	University of Pisa, Pisa, Italy	Pilot scale	Co-gasification of WSS and WP LHV:5.79 MJ/Nm^3 dry	[211]
Fixed bed reactor	Dokuz Eylul University, Izmir, Turkey	Pilot scale	1kW of electricity was produced Gasification of SS	[252]
Bubbling fluidized bed reactor	University of Stuttgart, Germany	Pilot scale	Capacity:20kW Co-gasification of SS with WP, SP, MN, CaO an additive	[235, 253]
Circulating fluidized bed reactor	Tokyo Bureau of Sewerage, Japan 2005	Demonstration Unit	15t/d of sewage sludge facility, 150kW electrical power, 55% reduction in GHG	[254]
Fixed bed reactor	Sanford. U.S.A	Commercial scale	1440 lbs/hr capacity and 10MM btu/hr of output energy	[255]
Ultra high temperature gasifier	Emmerich, Germany	Demonstration unit	1 TPD capacity, 12.6 kW electrical output	[255]
Fixed bed reactor	Suranaree University of Technology, Thailand	Pilot scale	Generated 85kW of electrical power	[212]

5.6 Super Critical Water Gasification (SCWG) for Sewage Sludge

Another growing technique to recover energy from dewatered sewage sludge is supercritical water gasification (SCWG) operating at 400-600°C, high pressure and long residence time, which produces gases similar to a conventional gasification system along with the potential for phosphorous recovery with other inorganic elements. Use of catalysts in SCWG may produce favorable results to add more value to the end-products [256]. Due to the use of high temperature and pressure, all the mineral content and heavy metal become concentrated in the residue and gives a potential for resource recovery. Phosphorous recovery using an uncatalyzed process is reported as 95% by using SCWG [257]. Though this process is being used for hydrogen production and extraction of inorganics, it involves high cost which does not lead it to be a viable commercial solution. In future, more studies are required for its viability.

5.7 Challenges for Gasification of Sewage Sludge

In this section, sewage sludge gasification has been discussed and compared with co-gasification and catalytic gasification. The key challenges for effective use of sewage sludge gasification are the following: (1) Due to high moisture and ash content the quality of gasification products is low. (2) Low LHV, CGE, CCE and tar content cause the problem of downstream utilization, for example, blocking of fuel lines in engines and lowered combustion quality in boilers. (3) Co-gasification with coal, woody biomass, straws, forestry wastes and manures improves the quality of syngas. However, appropriate blending ratios and operating conditions make improvement in one parameter for example high hydrogen yield but at the same time more tar in syngas and solid residues is problematic. (4) Co-gasification with coal may help to reduce the GHG emissions, nonetheless, high ash and heavy metal content would affect the overall efficiency. (5) Use of catalysts in sewage sludge gasification and co-gasification have shown promising results such as, hydrogen yield at up to 51 vol.%, tar yield reduced to 95% and LHV improved to 9MJ/Nm^3. The coke formation, resulting in early deactivation of active pore sites on the catalyst is challenging to maintain the continuous improved gas yields with high energy content. (6) Nitrogenous compounds are present in gas, char and ash of sewage sludge, which leads to GHG emissions and toxicity in the ash if it is to be utilized in land and agriculture applications. In tar, there are also nitrogenous compounds present such as, amines and pyrroles which can lead to ammonia and HCN and results in GHG emissions. Co-gasification and catalytic gasification helps to reduce nitrogenous compounds and converts them into N_2 to some extent, however more in-depth studies are needed for sewage sludge. (7) Similarly, sulfur content in gas, char, ash and tar is inevitable and challenging to decrease by using suitable catalysts. Iron and calcium salts provide encouraging results which can be improved more with further studies. (8) Suitable selection of catalysts for reduction of pollutants and tar is challenging due to the high ash content of sewage sludge which affects the product quality and also regeneration issues of catalysts are difficult. (9) It has been seen that for pilot, demonstration and commercial scale plants in different countries are not using any catalyst except calcium oxide because of coke formation and regeneration issues due to the high ash content of sewage sludge. Use of catalysts has been found in several laboratory scale studies which gave encouraging results to test in commercial and large scale plants. The catalyst combinations other than Ni-A.C, natural catalysts (dolomite and olivine) or char from pyrolysis, like Co-Mo, Co-Ce, zeolites and perovskites are challenging for sewage sludge gasification. However, more studies are required for their trials. (10) Ash agglomeration and clinker formation at the grate of the reactor and methods for ash removal from the reactor is challenges in selection of reactor technology. Syngas cleaning using appropriate catalyst or additive filters, liquid or dry filters is also a key issue. (11) If sewage sludge is being directly fed into the gasifier, the consumption of energy for drying is a major issue, otherwise using pyrolytic char as the feed stock is promising for gasification reactions in the presence of steam and air. (12) The recovery of P, N and K from ash is also a potential challenge for a circular economy, environmental and social problems associated with sewage sludge.

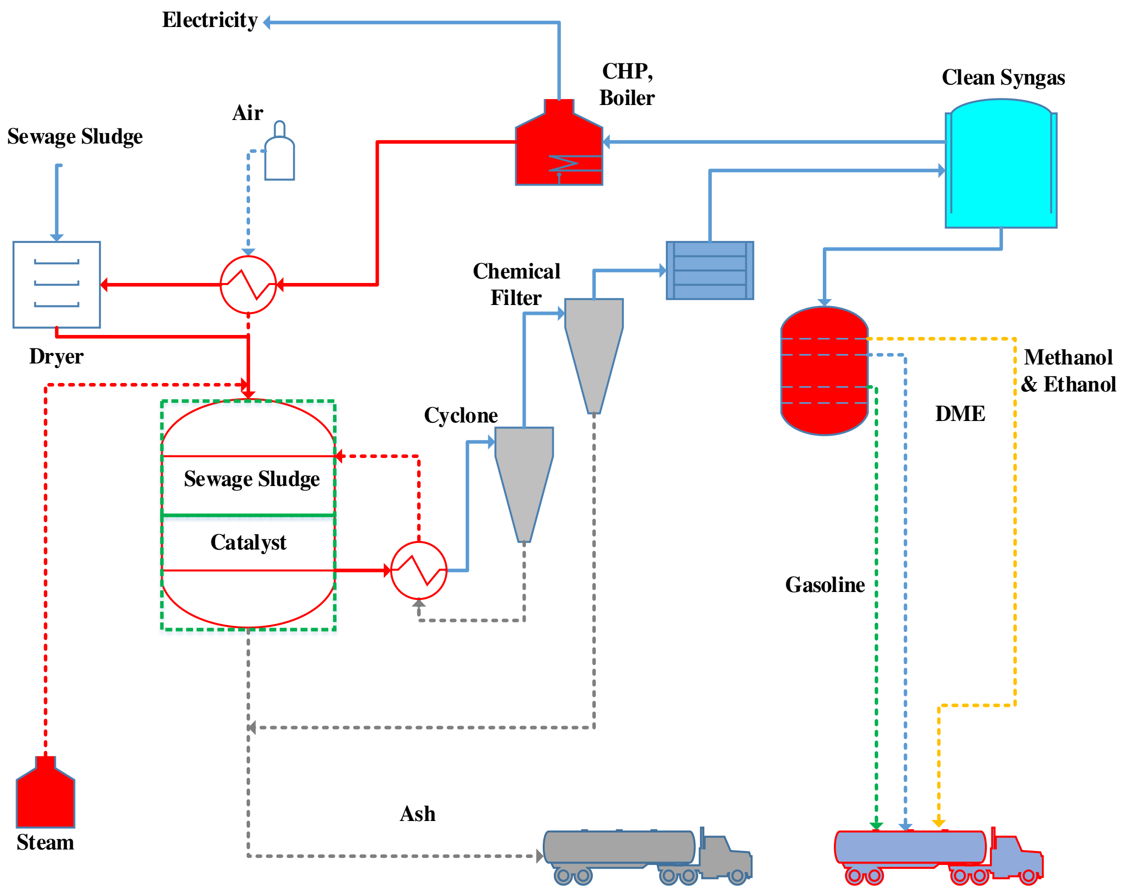


Fig. 24: Process flow diagram for sewage sludge gasification and its products.

6. Combustion of Sewage Sludge

This section concerns the oxidation of sewage sludge in the presence of excess oxygen. The combustion of sewage sludge is in general terms similar to other solid fuels. The excess oxygen provided acts to combust all carbon and volatile compounds at temperatures typically greater than 1000°C. In the context of sewage sludge combustion, there are three main aspects, to generate heat and power, to eliminate the effect of hazardous compounds present in the sewage sludge and to reduce the volume of sewage sludge [190, 258]. The main three products of combustion are flue gas, slag and fly ash [259]. Some systems are only developed to obtain heat and power generation, but along with heat, some hazardous contaminants in the form of flue gases containing CO_2, CO, CH_4, NOx, SOx, PAHs and dioxins/furans are emitted which can cause serious health and environmental issues. Fly ash or bottom ash contain numerous materials which can be exploited for utilization in other applications for example, sewage sludge may contain phosphorous for use as a nutrient in agricultural applications.

6.1 Development of Incinerators for Sewage Sludge

During the combustion of sewage sludge, the generated flue gas must be clean to ensure compliance with regulated emission limits. Factors which affect the flue gas pollutant composition are, the nature of the feedstock, the temperature inside the incinerator for drying, pyrolysis and combustion, flue gas flow rates and temperature. Apart from this, heat transfer rates, proper reduction of char or feedstock or appropriate ash disposal systems (manual or automatic) are of great importance during the incineration process. In the particular case of sewage sludge, moisture content is high and therefore there is a requirement for pre-drying or use of hot air for drying inside the incinerator. In addition, the high ash content of sewage sludge would produce an increasing bed height, particularly for fluidized bed combustion, which can disturb the whole combustion process and may create problems while cleaning of the gas due to high fly ash content. Hence, the selection of incinerator design has vital importance in the combustion process. In this regard, several incinerator technology designs have been reported for sewage sludge for example multiple hearth, fluidized bed, rotary kiln and other furnace types [260-263]. The design of multiple hearth incinerators contains several hearths as the name suggests, which are attached to a rotating shaft and enables feeding of the sludge from the top to the bottom in drying, pyrolysis and combustion zones. Old style multiple hearths had a problem of insufficient drying in the upper zone and combustion at lower zones. Later on, engineers added additional fuel lines to increase the efficiency of mixing, drying and combustion at their respective zones. Fluidized beds have received much more recent attention and in a very short time a large number of these design of incinerators have been used for sewage sludge combustion. Fluidized beds (bubbling and circulating) have the same design as discussed for pyrolysis and gasification, typically comprising a bed of sand. The hot fluidizing air helps to maintain good heat transfer rates with attrition of fuel particles until complete reduction and combustion. The internal designs may vary including spout formation inside the fluidized bed or circulating fluidized beds. Rotary kilns are also used for combustion of sewage sludge in small to medium scale incinerators. This furnace kiln type comprises a large steel vessel, often lined with ceramic materials which rotates slowly while completing combustion for flue gas. Heat transfer in the rotary kiln is lower as compared to multiple hearths and fluidized beds due to poorer mixing and infrequent contact of the waste with the hot wall which results in incomplete vapor formation leaving higher levels of char. In order to assess the life cycle assessment for combustion of sewage sludge in a fluidized bed combustor and rotary kiln, the fluidized bed combustor is reported to be better in terms of environmental sustainability rather than the rotary kiln [264]. Other furnaces have been used for incineration of sewage sludge such as combining multiple hearth and fluidized bed, cyclone furnaces, and for co-firing of sewage sludge and coal in pulverized form.

6.1.1 Technological Strength and Market Competitiveness of Incinerators

The technological strength of incinerators can be descried by evaluating them using the Analytical Hierarchy Process (AHP). There are three main incinerators for which technological strength and market competitiveness may be analyzed. Higher heat transfer is a desirable parameter which gives more drying, pyrolysis and combustion of char resulting in more flue gas and reduction in solid residues. In this regard, fluidized bed incinerators are proven for these parameters. Particularly for sewage sludge, the ash content is higher and it may increase the bed height and also ash disposal is a key consideration. Rotary kilns due to moving and conveying fuel in the forward direction at a particular angle seems better for less ash disposal problems, however they have low heat transfer rates. Table 21 shows the technological strength of incinerators and Fig. 25 illustrates the relation of technological strength and market competitiveness. Most positive attribute (flue gas throughput) is shown as a higher value 10, and the most negative attribute is ash disposal.

Table 21: Technological strength of sewage sludge incinerators.

Reactors	Flue gas	Scale up	Complexity	Heat transfer	Ash disposal	T.S
Multiple hearth	6	10	3	6	3	28
FBC	10	10	3	10	6	39
Rotary	6	10	6	3	6	31

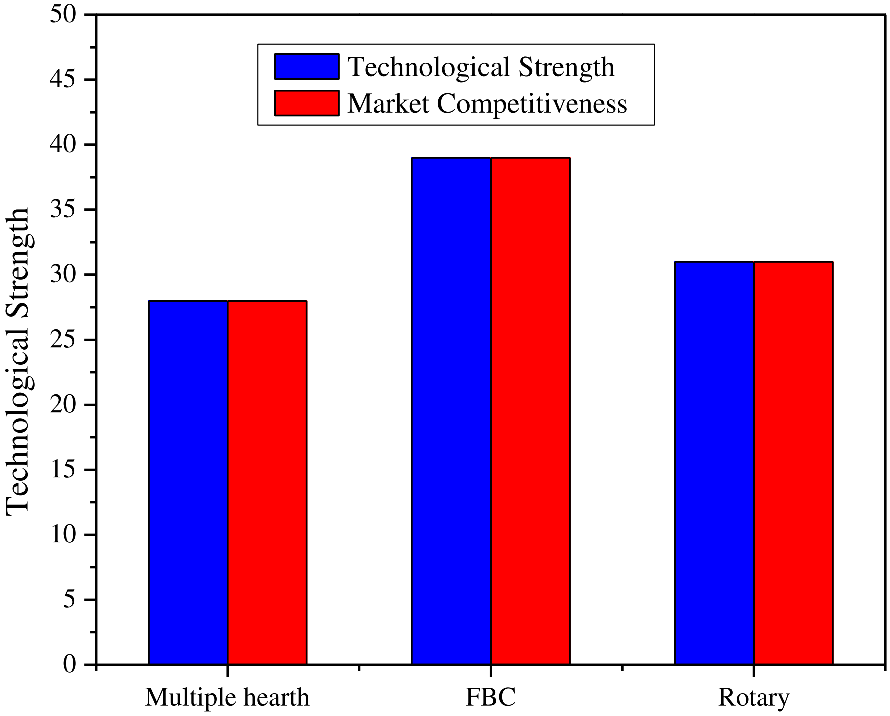


Fig. 25: Technological strength and market competitiveness of sewage sludge incinerators.

6.2 Flue Gas Cleaning Systems and Pollutant Emissions

The flue gas from a sewage sludge incinerator consists of particulates, NOx, SOx, heavy metals, PAHs, PCDD/PCDF, etc. [265-268]. To reduce these pollutants, sewage sludge can be co-combusted with coal and biomass within the incinerator [259, 269]. The reason to use coal [266, 270, 271] and biomass (wood pellets [261, 272], forestry waste [273]) as added fuels with sewage sludge combustion is to avoid agglomeration and de-fluidization due to higher content of ash [274, 275]. Another way to reduce these noxious compounds are scrubbers or filters. After the incinerator furnace, a boiler can produce steam for electricity and to pre-heat the inlet air and drying of sewage sludge. Cyclones help to extract unburnt char, ash and dust particles which may be recycled to the incinerator for further combustion. An electrostatic precipitator may be used to extract the dust particles and fly ash in the flue gas left after the cyclones. Sulphur oxides may be removed by scrubbers using for example, $Ca(OH)_2$, also NOx can be reduced by addition of ammonium hydroxide or urea. Metals such as Cd and Hg and dioxins and furans (PCDD and PCDF) can be controlled by addition of activated carbon with downstream fabric filter capture [276]. It has also been reported that adding CaO with sewage sludge and coal can improve the performance for devolatalization, desulfurization and denitrification for clean disposal of sewage sludge. The addition of CaO also helps in lowering the temperature for combustion [277-279]. The combination of $FeCl_3$ and CaO with combustion is reported favorably to reduce the emissions of SO_2, HCl and heavy metals such as Pb, Zn and Cu [280]. If sewage sludge is being disposed of in cement kilns, then there is a chance of more sulfur emissions which can be reduced by using suitable co-feedstock or scrubbers/ filters [281]. Several studies are found in the literature which report decreased emissions to minimum levels. The investment cost for incinerators is estimated at 700-1500€ / dry ton of sewage sludge and its operational and maintenance cost is estimated at 250-300 €/dry ton of sewage sludge [282]. This higher cost is due to extensive cleaning of gas systems and emissions control.

6.3 Sewage Sludge Ash from Combustion

Sewage sludge ash is produced in significant quantities derived as a by-product from the combustion of sewage sludge mainly through its use as an auxiliary fuel in the cement industry. Several studies have explored and determined using life cycle assessments, tangible environmental paybacks by using sewage sludge ash as a supplementary cementitious material [283]. For the continued usage of sewage sludge ash as a building material, there must be sufficient risk assessments to avoid the hazardous effects of heavy metals which could be potentially released into the environment during the utilization of the product materials. Researchers have analyzed the results from laboratory and field tests on the leaching of sewage sludge ash being used in applications such as concrete, road pavements, blocks, clinker production, mortar, road pavements, geo-technics and ceramics [284]. In Table 22 a comparison of elemental analyses is made between bottom ash and fly ash produced from the combustion of sewage sludge together with limit values. The values for the ash deviate and indicate that it could be used as a fertilizer material after suitable treatment and extraction to prevent environmental impacts from its application. The range of mineral contents in sewage sludge ash, coal sludge ash and cement are given in Table 23, which illustrates the requirement for cement manufacturing can be fulfilled by sewage sludge ash to some extent.

Table 22: Comparison of trace elements in sewage sludge bottom ash, fly ash and limit values.

Element (mg/kg)	Bottom Ash[285]	Fly Ash[285]	Limit Values[286]
As	10.5	82.5	1×10^{-4}
Cd	1.3	47.9	5×10^{-4}
Hg	<0.1	0.16	1×10^{-4}
Ni	466.8	766.8	0.022
Pb	78	111.2	1×10^{-3}

Ba	712	915	4 x 10^{-3}
Co	41.8	68.1	n. r
Cr	279.5	513.8	5 x 10^{-4}
Cu	1284.5	2657.3	2 x 10^{-3}
Mo	26.9	31.6	n. r
Sb	2.1	4.1	n. r
Zn	4249.8	9124.5	7 x 10^{-3}

Table 23: Contents in sewage sludge ash, coal fly ash and cement [287, 288].

Contents (%)	Sewage Sludge Ash [287, 288]	Coal Fly Ash [287]	Cement [287]
MgO	0.02-23.4	0.1-6.7	0.53
Al_2O_3	4.4-34.2	2.6-20.5	4.91
SiO_2	14.4-65	11.8-46.4	20.1
CaO	1.1-40.1	15.1-54.8	65.8
TiO_2	0.3-1.9	0.6-1.0	0.35
Fe_2O_3	2.1-30	1.4-15.6	5.43
MnO	0.03-0.9	0.1-6.7	0.04
K_2O	0.1-3.1	0.3-9.3	0.81
Na_2O	0.01-6.8	0.2-2.8	< 0.67
P_2O_5	0.3-26.7	0.2-0.4	0.23
SO_3	0.01-12.4	1.4-12.9	4.74
CO_2	10.37 ± 0.04	n. r	n. r

Thus, the drawback of the combustion process is the production of ash with the potential for emission of hazardous compounds. Co-combustion has been undertaken in practice and has shown promising results. As compared to deploying ash for agriculture purposes directly, it is better to be used in cement plants to avoid environmental issues. A schematic diagram for sewage sludge combustion is presented in Fig. 26.

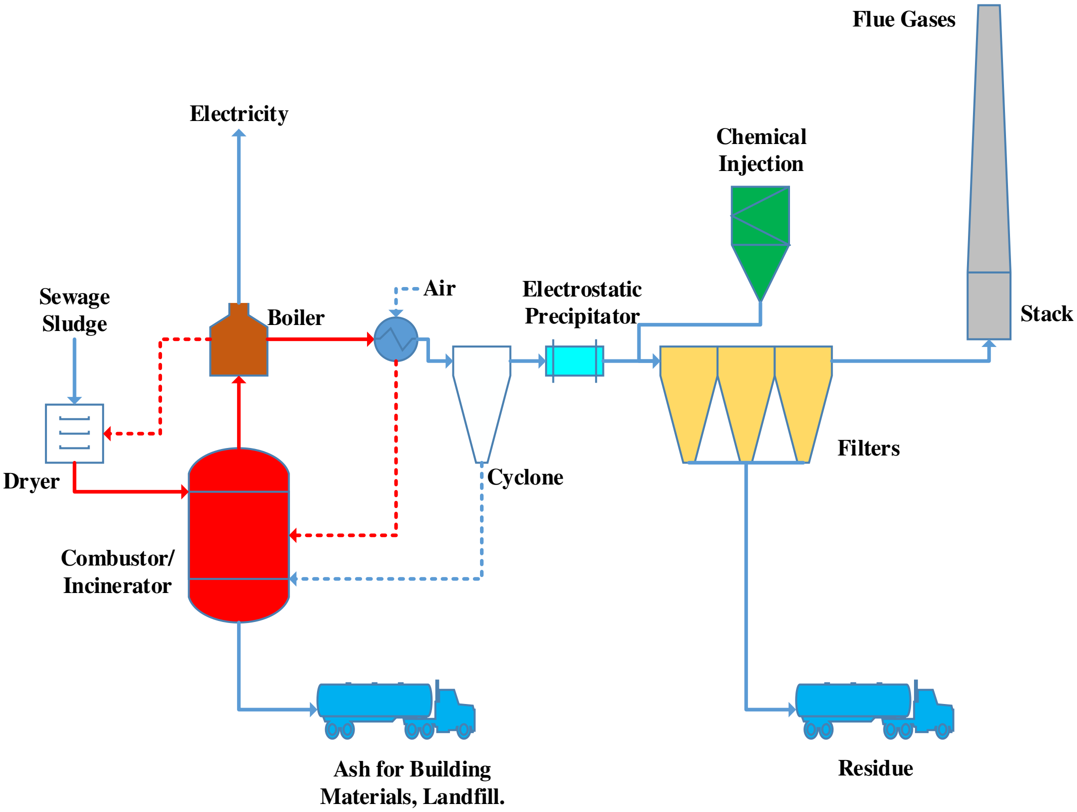


Fig. 26: Schematic diagram of sewage sludge combustion.

7. Conclusions

It may be concluded that despite having high moisture content, ash content and heavy metal content, thermochemical routes are promising for the management of sewage sludge for the recovery of energy. This review has produced a comprehensive comparison of pyrolysis, gasification and incineration of sewage sludge. Also considered are co-processing and the use of catalysts. The pollutant emissions are considerably less for pyrolysis while enabling the production of a bio-oil and char for heating and further use. Torrefied char, pyrolytic char and hydro char have potential as catalysts or adsorbents. Gasification, co-gasification and catalytic gasification of sewage sludge also showed production of high quality syngas. Comparative analysis of pyrolysis and gasification coupled with catalytic processes have been shown to be efficient to deal with the pollutants and produce energy products. Due to the high level of pollutant contamination present in sewage sludge, combustion or incineration does not appear attractive from an environmental and socio-economic point of view. It produces more pollutants in the flue gases and ash, resulting in high operational and maintenance cost as compared to pyrolysis and gasification. While recovery of phosphorous and use of ash in agriculture and in the construction industry has the potential for positive impacts on the environment and economic evaluation. Conversely, ash to be applied in these applications must meet the legal regulations which is far better and more environmentally sustainable than raw sewage sludge usage in landfill and agriculture. Ideally, in terms of the circular economy, sewage sludge becomes zero waste material producing energy (syngas and bio-oil), a wide range of valuable products and recovery of phosphorous, nitrogen, and potassium present in considerable amount.

8. Future Prospects and Recommendations

The most important factors to suggest for sewage sludge are the need for innovations in pre-treatment, process intensification, sludge valorization, resource recovery, energy recovery and costs. Thermochemical processes appear better than other conventional techniques due to the above mentioned factors. However, a key consideration is the Technology Readiness Level (TRL), for example for pyrolysis technologies, TRL levels are low (4-5) resulting in less commercial viability. The reason is, the main products are char and bio-oil which are not ready for commercial use except perhaps use in gasification or heating oil after upgrading. As the pyrolysis is carried out at lower temperatures than gasification and combustion, so the high moisture content influences the bio-oil composition and char quality. Bio-oil upgrading seems attractive due to the bio-oil having physio-chemical properties near to heavy fuel oil, yet co-pyrolysis or addition of catalyst is needed for that purpose. Use of catalysts and combinations of catalysts may help to upgrade pyrolytic oil to be used commercially. Similarly, chars for use as catalysts or adsorbents are promising, nonetheless their activation is required for commercial usage. Thus three aspects: pretreatment, energy recovery and resource recovery are suggested for pyrolysis for further study. While exploring research articles and reports at internet level, rarely were commercial facilities for pyrolysis of sewage sludge found. On the other hand, many commercial and pilot plant entities for sewage sludge gasification have been listed in this manuscript, showing energy recovery (syngas) and resource recovery (P, N and other minerals). The process intensification has been shown with co-gasification, which can be more improved by using catalysts. Although catalysts would add cost in the operation and regeneration process, their use results in an increase in syngas energy level and mitigation of pollutants which would be advantageous. In this manuscript, a number of catalysts and additives are listed which have been applied in-situ and ex-situ at laboratory scale level. This concept can be perceived to enhance the efficiency of the sewage sludge gasification process at pilot, demonstration or commercial scale. The addition of catalysts in the sewage sludge gasification process would be helpful to uplift the TRL value from 6 to 9. Increase in TRL value means, it would be very easy for investors to invest capital in sewage sludge gasification. Process intensification, sludge reduction and energy recovery is related to syngas and chemicals production, while resource recovery is associated with the heavy metals and minerals content present in gasification ash. The pollutant emissions during sewage sludge are found with more nitrogen and sulfur content and the use of catalysts and additives are helpful to reduce NOx and SOx. Hence, catalytic gasification is promising for technological development, alleviation of pollutants for environmentally friendly produced products and addition of social-economic benefits. The pure and clean syngas would be combusted with coal /other fuels, contributing towards reducing the load/burden on fossil fuels and a definite positive impact on the circular economy.

Reactor technologies for thermochemical options have a vital role to play. Operational parameters and design of reactors during the process have a great influence on the product quality. Sometimes, a reactor may have one most attributed positive quality but at the same time the sum of many other negative aspects may be present which can make it less appropriate on technological strength and certainly in terms of market competitiveness. The analysis carried out in this manuscript on the reactor technologies in thermochemical processing routes are recommended. It may help to intensify the process for value added products. In the future, more detailed studies are required on the barriers (high moisture, ash and heavy metal content) to enhance the products quality and to make them readily available for commercial purposes.

Acknowledgement

The authors would like to appreciate the support of the National Natural Science Foundation of China (No. 51476023, 51306029), Key Program for China EU International Cooperation in Science and Technology Innovation (No. 2018YFE0173), Shaanxi Provincial Natural Science Foundation Research Program-Shaanxi Coal Joint Funding (2019JLZ-12), Key Research and Development Plan of Shaanxi Province (2017GY-167), and China Postdoctoral Science Foundation (2016M600790, 2016M602828).

References

[1] Quanguo Zhang JH, Duu-Jong Lee , Yingju Chang, Yu-Jen Lee. Sludge treatment: Current research trends. Bioresource Technology 243 (2017) 1159–1172.

[2] Sung Hee Joo FDM, Eric Antmann, Philip Chorath. Sustainable approaches for minimizing biosolids production and maximizing reuse options in sludge management: A review. Journal of Environmental Management 158 (2015) 133-145.
[3] Abdul Raheem VSS, Jun He, Wafa Dastyar, Dionysios D. Dionysiou, Wei Wang, Ming Zhao. Opportunities and challenges in sustainable treatment and resource reuse of sewage sludge: A review. Chemical Engineering Journal 337 (2018) 616–641.
[4] Małgorzata Kacprzak EN, Krzysztof Fijałkowski, Anna Grobelak, Anna Grosser, Małgorzata Worwag, Agnieszka Rorat, Helge Brattebo, Åsgeir Almås, Bal Ram Singh. Sewage sludge disposal strategies for sustainable development. Environmental Research 156 (2017) 39–46.
[5] QilinWang WW, Yanyan Gong, Qiming Yu, Qin Li, Jing Sun, Zhiguo Yuan. Technologies for reducing sludge production in wastewater treatment plants: State of the art. Science of the Total Environment 587–588 (2017) 510–521.
[6] Xiao Lisha LT, Wang Yin, Ye Zhilong, Liao Jiangfu. Comparative life cycle assessment of sludge management: A case study of Xiamen, China. Journal of Cleaner Production 192 (2018) 354-363.
[7] Guang Yang GZ, Hongchen Wang. Current state of sludge production, management, treatment and disposal in China. Water Research 78 (2015) 60-73.
[8] Ali Zaker ZC, Xiaolei Wang, Qiang Zhang. Microwave-assisted pyrolysis of sewage sludge: A review. Fuel Processing Technology 187 (2019) 84–104.
[9] Ying-Chu Chen JK. Potential of greenhouse gas emissions from sewage sludge management: a case study of Taiwan. Journal of Cleaner Production 129 (2016) 196-201.
[10] Xiao-Pei Zhang CZ, Xin Li, Sheng-Hui Yu, Peng Tan, Qing-Yan Fang, Gang Chen. A two-step process for sewage sludge treatment: Hydrothermal treatment of sludge and catalytic hydrothermal gasification of its derived liquid. Fuel Processing Technology 180 (2018) 67–74.
[11] Marie Collard BT, Laurent Lemee. Comparison of three different wastewater sludge and their respective drying processes: Solar, thermal and reed beds e Impact on organic matter characteristics. Journal of Environmental Management 203 (2017) 760-767.
[12] Richard Wickham SX, Brendan Galway, Heriberto Bustamante, Long D. Nghiem. Anaerobic digestion of soft drink beverage waste and sewage sludge. Bioresource Technology 262 (2018) 141–147.
[13] S. Zahedi MR, R. Solera, M. Perez. Mesophilic anaerobic co-digestion of sewage sludge with glycerine: Effect of solids retention time. Fuel 215 (2018) 285–289. 2018.
[14] Guangyin Zhen XL, Hiroyuki Kato, Youcai Zhao, Yu-You Li. Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: Current advances, fullscale application and future perspectives. Renewable and Sustainable Energy Reviews 69 (2017) 559–577.
[15] Krzysztof Fijalkowski AR, Anna Grobelak, Malgorzata J. Kacprzak. The presence of contaminations in sewage sludge:The current situation. Journal of Environmental Management 203 (2017) 1126-1136.
[16] Xingdong Wang CL, Bin Zhang, Jingjiang Lin, Qiaoqiao Chi, Yin Wang. Migration and risk assessment of heavy metals in sewage sludge during hydrothermal treatment combined with pyrolysis. Bioresource Technology 221 (2016) 560–567.
[17] A. Gianico CMB, G. Mascolo, G. Mininni. Partitioning of nutrients and micropollutants along the sludge treatment line: a case study. Environ Sci Pollut Res (2013) 20:6256–6265.

[18] Anjali Mulchandani PW. Recovery opportunities for metals and energy from sewage sludges. Bioresource Technology 215 (2016) 215–226.

[19] Kandasamy Jayaraman IG. Pyrolysis, combustion and gasification characteristics of miscanthus and sewage sludge. Energy Conversion and Management 89 (2015) 83–91.

[20] Andreea Gherghel CT, Sabino De Gisi. A review on wastewater sludge valorisation and its challenges in the context of circular economy. Journal of Cleaner Production 228 (2019) 244-263.

[21] Xiaoji Liu FC, Cuiping Wang, Zhengyu Jin, Jing Wu, Jiane Zuo, Kaijun Wang. Pyrolysis and subsequent direct combustion of pyrolytic gases for sewage sludge treatment in China. Applied Thermal Engineering 128 (2018) 464–470.

[22] Young-Kon Choi J-HK, Joo-Sik Kim. Gasification of dried sewage sludge using an innovative three-stage gasifier: Clean and H2-rich gas production using condensers as the only secondary tar removal apparatus. Fuel 216 (2018) 810–817.

[23] Ningbo Gao ZL, Cui Quan, Norbert Miskolczi, Attila Egedy. A new method combining hydrothermal carbonization and mechanical compression in-situ for sewage sludge dewatering: Bench-scale verification. Journal of Analytical and Applied Pyrolysis 139 (2019) 187-195.

[24] Munsik Park NK, Sunkyung Lee, Seungjae Yeon, Ji Hae Seo, Donghee Park. A study of solubilization of sewage sludge by hydrothermal treatment. Journal of Environmental Management 250 (2019) 109490.

[25] Isabel Fonts GG, Manuel Azuara, Javier Ábrego, Jesús Arauzo. Sewage sludge pyrolysis for liquid production: A review. Renewable and Sustainable Energy Reviews 16 (2012) 2781– 2805.

[26] Syed Shatir A. Syed-Hassan YW, Song Hu, Sheng Su, Jun Xiang. Thermochemical processing of sewage sludge to energy and fuel: Fundamentals, challenges and considerations. Renewable and Sustainable Energy Reviews 80 (2017) 888–913.

[27] P. Manara AZ. Towards sewage sludge based biofuels via thermochemical conversion – A review. Renewable and Sustainable Energy Reviews 16 (2012) 2566– 2582.

[28] Yucheng Cao AP. Sewage sludge-to-energy approaches based on anaerobic digestion and pyrolysis: Brief overview and energy efficiency assessment. Renewable and Sustainable Energy Reviews 16 (2012) 1657– 1665.

[29] Hugo Perazzini FBF, Fábio Bentes Freire & José Teixeira Freire. Thermal Treatment of Solid Wastes Using Drying Technologies: A Review. Drying Technology 2016, Vol 34, No 1, 39–52.

[30] Cesar Huilinir MV. Simultaneous effect of initial moisture content and airflow rate on biodrying of sewage sludge. Wtaer Research 82 (2015) 118-128.

[31] Lu Cai TK, Tong-Bin Chen, Ding Gao, Li Wan. Structure modification and extracellular polymeric substances conversion during sewage sludge biodrying process. Bioresource Technology 216 (2016) 414–421.

[32] Qian Li XL, Haigang Guo, Zengjun Yang, Yingte Li, Suli Zhi, Keqiang Zhang. Sewage sludge drying method combining pressurized electro-osmotic dewatering with subsequent bio-drying. Bioresource Technology 263 (2018) 94–102.

[33] Boran Wu KH, Devinder Mahajan, Xiaoli Chai, Dianhai Yang, Xiaohu Dai Free-conditioning dewatering of sewage sludge through in situ propane hydrate formation. Water Research 145 (2018) 464-472.

[34] Mohamed Hédi Romdhana DL, Bruno Ladeviea, Caroline Sablayrolles. Monitoring of pathogenic microorganisms contamination during heat drying process of sewage sludge. Process Safety and Environmental Protection 87 (2009) 377-386.

[35] Bennamoun L. Solar drying of wastewater sludge: A review. Renewable and Sustainable Energy Reviews 16 (2012) 1061– 1073.

[36] Ivan Deviatkin LL, Shaoqing Chen, Jouni Havukainen, Fei Wang, Mika Horttanainen, Mika Mänttäri. Technical implications and global warming potential of recovering nitrogen released during continuous thermal drying of sewage sludge. Waste Management 90 (2019) 132–140.

[37] Yongjie Xue CW, Zhenhua Hu, Yi Zhou, Gang Liu, Haobo Hou, Yue Xiao, Teng Wang, Jinping Li. Thermal treatment on sewage sludge by electromagnetic induction heating: Methodology and drying characterization. Waste Management 78 (2018) 917–928.

[38] Lu Cai T-BC, Ding Gao, Jie Yu. Bacterial communities and their association with the bio-drying of sewage sludge. Water Research 90 (2016) 44-51.

[39] Marco Tomasi Morgano HL, Frank Richter, Dieter Stapf, Helmut Seifert. Screw pyrolysis technology for sewage sludge treatment. Waste Management 73 (2018) 487–495.

[40] R. Mailler JG, G. Chebbo, V. Rocher. Priority and emerging pollutants in sewage sludge and fate during sludge treatment. Waste Management 34 (2014) 1217–1226.

[41] Sicco H. Brandsma LvM, Jake W. O'Brien, Geoff Eaglesham, Pim. E. G. Leonards,Jacob de Boer, Christie Gallen,Jochen Mueller, Caroline Gaus,and Christian Bogdal. Medium-Chain Chlorinated Paraffins (CPs) Dominate in Australian Sewage Sludge. Environ Sci Technol 2017, 51, 3364−3372.

[42] Noriatsu Ozaki AN, Kazuki Nakashima, Tomonori Kindaichi, Akiyoshi Ohashi. Loading and removal of PAHs, fragrance compounds, triclosan and toxicity by composting process from sewage sludge. Science of the Total Environment 605–606 (2017) 860–866.

[43] Ville Turunen JS, Anna Mikola. A decision support tool for selecting the optimal sewage sludge treatment. Chemosphere 193 (2018) 521-529.

[44] F.J.Camino-Sánchez AZ-G, N.Dorival-García, B.Juárez-Jiménez, J.L. Vílchez. Determination of selected parabens, benzophenones, triclosan and triclocarban in agricultural soils after and before treatment with compost from sewage sludge: Alixiviation study. Talanta 150 (2016) 415–424.

[45] Elzbieta Wołejko UW, Agata Jabłonska-Trypu, Andrzej Butarewicz, Tadeusz Łobod. The effect of sewage sludge fertilization on the concentration of PAHs in urban soils. Environmental Pollution 232 (2018) 347-357.

[46] Wen Fang GQ, Yonghong Wei, David S. Kosson, Hans A. van der Sloot, Jianguo Liu. Leaching characteristic of toxic trace elements in soils amended by sewage sludge compost: A comparison of field and laboratory investigations. Environmental Pollution 237 (2018) 244-252.

[47] Maria Muñoz MAG, M. Francisca Gomez-Rico, Rafael Font. PCDD/F determination in sewage sludge composting. Influence of aeration and the presence of PCP. Science of the Total Environment 616–617 (2018) 763–773.

[48] Shen Guo JL, Qingping Wang, Mallavarapu Megharaj, Zuliang Chen. The toxicity of graphene and its impacting on bioleaching of metal ions from sewages sludge by Acidithiobacillus sp. Chemosphere 195 (2018) 90-97.

[49] Yang Guo-hang ZG-y, Li He-lian, Han Xue-mei, Li Ju-mei, Ma Yi-bing. Accumulation and bioavailability of heavy metals in a soil-wheat/ maize system with long-term sewage sludge amendments. Journal of Integrative Agriculture 2018, 17(8): 1861–1870.

[50] Camila Pesci Pereira TdCP, Giselle Gomes, Bianca Ramalho Quintaes, Daniele Maia Bila, Juacyara Carbonelli Campos. Evaluation of reduction estrogenic activity in the combined treatment of landfill leachate and sanitary sewage. Waste Management 80 (2018) 339–348.

[51] Chengdu Qi JH, Bin Wang, Shubo Deng, Yujue Wang, Gang Yu. Contaminants of emerging concern in landfill leachate in China: A review. Emerging Contaminants (2018) 1-10.

[52] Cintia Flores a FVb, Jordi Martin-Alonso c, Josep Caixach. Occurrence of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in N.E. Spanish surface waters and their removal in a drinking water treatment plant that combines conventional and advanced treatments in parallel lines. Science of the Total Environment 461–462 (2013) 618–626.

[53] D. Zacs VB. Trace determination of perfluorooctane sulfonate andperfluorooctanoic acid in environmental samples (surface water,wastewater, biota, sediments, and sewage sludge) using liquidchromatography – Orbitrap mass spectrometry. Journal of Chromatography A, 1473 (2016) 109–121.

[54] Hong Chen CZ, Jianbo Han, Yixuan Yu, Peng Zhang. PFOS and PFOA in influents, effluents, and biosolids of Chinese wastewater treatment plants and effluent-receiving marine environments. Environmental Pollution 170 (2012) 26-31.

[55] Hanna Ulrich KPF, Michael Gierig. Getting on with persistent pollutants: Decreasing trends of perfluoroalkyl acids (PFAAs) in sewage sludge. Chemosphere 161 (2016) 527-535.

[56] Jack Thompson GE, Julien Reungoat, Yvan Poussade, Michael Bartkow, Michael Lawrence, Jochen F. Mueller. Removal of PFOS, PFOA and other perfluoroalkyl acids at water reclamation plants in South East Queensland Australia. Chemosphere 82 (2011) 9–17.

[57] Voet ACAJvd. Occurrence and point source characterization of perfluoroalkyl acids in sewage sludge. Chemosphere 129 (2015) 62–73.

[58] Lucia Ivanová TM, Roman Grabic, Oksana Golovko, Olga Kob, Andrea Vojs Staňová, Petra Szabová, Anna Grenčíková, Igor Bodík. Pharmaceuticals and illicit drugs – A new threat to the application of sewage sludge in agriculture. Science of the Total Environment 634 (2018) 606–615.

[59] Paula Arbeláez FB, Rosa Maria Marcé, Eva Pocurull. Trace-level determination of sweeteners in sewage sludge usingselective pressurized liquid extraction and liquidchromatography–tandem mass spectrometry. Journal of Chromatography A, 1408 (2015) 15–21.

[60] Arjun K. Venkatesan RUH. National inventory of alkylphenol ethoxylate compounds in U.S. sewage sludges and chemical fate in outdoor soil mesocosms. Environmental Pollution 174 (2013) 189-193.

[61] Laura Martín-Pozo BdA-G, Rocío Rodríguez-Gómez, María Teresa García-Córcoles, Morsina Çipa, Alberto Zafra-Gómez. Analytical methods for the determination of emerging contaminants in sewage sludge samples. A review. Talanta 192 (2019) 508–533.

[62] N. Perez-Lemus RL-S, S.I. Perez-Elvira, E. Barrado. Analytical methodologies for the determination of pharmaceuticals and personal care products (PPCPs) in sewage sludge: A critical review. Analytica Chimica Acta 1083 (2019) 19-40.

[63] Fytili D. Utilization of sewage sludge in EU application of old and new methods-A review. Renewable and Sustainable Energy Reviews 12 (2008) 116–140.

[64] Qiao Xiong MZ, Mengjia Liu, Shijie Jiang, Haobo Hou. The transformation behaviors of heavy metals and dewaterability of sewage sludge during the dual conditioning with Fe2-sodium persulfate oxidation and rice husk. Chemosphere 208 (2018) 93-100.

[65] Hua-jun Huang X-zY. The migration and transformation behaviors of heavy metals during the hydrothermal treatment of sewage sludge. Bioresource Technology 200 (2016) 991–998.

[66] Xiangdong Meng QH, Huaping Gao, Kangrou Tay, Jianhua Yan. Improved utilization of phosphorous from sewage sludge (as Fertilizer) after treatment by Low-Temperature combustion. Waste Management 80 (2018) 349–358.
[67] T. Ahmad KA, M. Alam. Sustainable management of water treatment sludge through 3‘R’ concept. Journal of Cleaner Production 124 (2016) 1-13.
[68] Patryk Oleszczuk HH. Comparison of sewage sludge toxicity to plants and invertebrates in three different soils. Chemosphere 83 (2011) 502–509.
[69] Tingting Shen YT, Xiao-Ying Lu, Zhe Meng. Mechanisms of copper stabilization by mineral constituents in sewage sludge biochar. Journal of Cleaner Production 193 (2018) 185-193.
[70] Vinay Kumar Tyagi S-L. Sludge: A waste or renewable source for energy and resources recovery. Renewable and Sustainable Energy Reviews 25 (2013) 708–728.
[71] Akash Pratim Bora DPG, Krishna Sandilya Durbha. Sewage sludge to bio-fuel: A review on the sustainable approach of transforming sewage waste to alternative fuel. Fuel 259 (2020) 116262.
[72] Xiaolei Zhang SY, Rajeshwar D. Tyagi,RaoY. Surampalli,J ose R. Valéro. Wastewater sludge as raw material for microbial oils production. Applied Energy 135 (2014) 192–201.
[73] Ashish Pathak MGD, T.R. Sreekrishnan. Bioleaching of heavy metals from sewage sludge: A review. Journal of Environmental Management 90 (2009) 2343–2353.
[74] Puchong Thipkhunthod VM, Pramoch Rangsunvigit, Boonyarach Kitiyanan, Kitipat Siemanond, Thirasak Rirksomboon. Predicting the heating value of sewage sludges in Thailand from proximate and ultimate analyses. Fuel 84 (2005) 849–857.
[75] Tao Kan VS, and Tim Evans. Effect of the Heating Rate on the Thermochemical Behavior and Biofuel Properties of Sewage Sludge Pyrolysis. Energy Fuels 2016, 30, 1564−1570.
[76] Junnan Wu YL, Yan Lin, Yunlong Tian, Xiaoqian Ma. Study on thermal decomposition kinetics model of sewage sludge and wheat based on multi distributed activation energy. Energy 185 (2019) 795-803.
[77] Gennady Gerasimov VK, Oleg Potapov, Grigory Dvoskin, Valentina Kornileva, Lyudmila Dudkina Pyrolysis of sewage sludge by solid heat carrier. Waste Management 87 (2019) 218–227.
[78] Huan Liu QZ, Hongyun Hu, Peng Liu, Xiaowei Hu, Aijun Li, Hong Yao. Catalytic role of conditioner CaO in nitrogen transformation during sewage sludge pyrolysis. Proceedings of the Combustion Institute 35 (2015) 2759–2766.
[79] Qiyong Xu ST, Jingchen Wang, Jae Hac Ko. Pyrolysis kinetics of sewage sludge and its biochar characteristics. Process Safety and Environmental Protection 115 (2018) 49-56.
[80] Yi-fan Zhang S-yZ, Qing Mao, Hao Li, Cai-wei Wang, Feng-hao Jiang, Jun-fu Lyu. Volatility and partitioning of Cd and Pb during sewage sludge thermal conversion. Waste Management 75 (2018) 333–339.
[81] Maria NilzaCorrêaMartins V, TatianadaSilvaSouza. Genotoxic and mutagenic effects of sewage sludge on higher plants. Ecotoxicology and Environmental Safety 124 (2016) 489–496.
[82] Magdalena Kończak PO. Application of biochar to sewage sludge reduces toxicity and improve organisms growth in sewage sludge-amended soil in long term field experiment. Science of the Total Environment 625 (2018) 8–15.
[83] Boruszko D. Research on the influence of anaerobic stabilization of various dairy sewage sludge on biodegradation of polycyclic aromatic hydrocarbons PAHs with the use of effective microorganisms. Environmental Research 155 (2017) 344–352.

[84] P. Verlicchi EZ. Pharmaceuticals and personal care products in untreated and treated sewage sludge: Occurrence and environmental risk in the case of application on soil- A critical review. Science of the Total Environment 538 (2015) 750–767.

[85] Chad A. Kinney ETF, Dana W. Kolpin, Mark R. Burkhardt, Steven D. Zaugg, Stephen L. Werner, Joseph P. Bossio, Mark J. Benotti. Bioaccumulation of Pharmaceuticals and Other Anthropogenic Waste Indicators in Earthworms from Agricultural Soil Amended With Biosolid or Swine Manure. Vol 42, No 6, 2008 / Environmental Science & Technology.

[86] Li WC. Occurrence, sources, and fate of pharmaceuticals in aquatic environment and soil. . Environ Pollut 187, 193–201.

[87] Jing Yu JH, Shuhei Tanak, Shigeo Fujii. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in sewage treatment plants. Water Research 43 (2009) 2399-2408.

[88] N. Mills PP, J. Farrow, R.B. Thorpe, N.F. Kirkby. Environmental & economic life cycle assessment of current & future sewage sludge to energy technologies. Waste Management 34 (2014) 185–195.

[89] Sari Piippo Maria Lauronen HP. Greenhouse gas emissions from different sewage sludge treatment methods in north. Journal of Cleaner Production 177 (2018) 483-492.

[90] Sebastian Werle RKW. A review of methods for the thermal utilization of sewage sludge: The Polish perspective. Renewable Energy 35 (2010) 1914–1919.

[91] Lidia Lombardi CN, Elena Bettazzi, Donatella Fibbi, Ennio Carnevale. Environmental comparison of alternative treatments for sewage sludge: An Italian case study. Waste Management 69 (2017) 365–376.

[92] M.C. Samolad AAZ. Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy management in Greece. Waste Management 34 (2014) 411–420.

[93] M. Atienza-Martínez IF, L. Lázaro, J. Ceamanos, G. Gea. Fast pyrolysis of torrefied sewage sludge in a fluidized bed reactor. Chemical Engineering Journal 259 (2015) 467–480.

[94] M. Atienza-Martínez IF, J. Ábrego, J. Ceamanos, G. Gea. Sewage sludge torrefaction in a fluidized bed reactor. Chemical Engineering Journal 222 (2013) 534–545.

[95] Ana Belen Hernández FO, Ntuli Freemana. Sewage sludge charcoal production by N2- and CO2-torrefaction. Journal of Environmental Chemical Engineering 5 (2017) 4406–4414.

[96] Jeeban Poudel T-IO, Sang-Hoon Lee, Sea Cheon Oh. A study on torrefaction of sewage sludge to enhance solid fuel qualities. Waste Management 40 (2015) 112–118.

[97] Javier Ábrego JLSn, Jesús Arauzo,Isabel Fonts, Noemí Gil-Lalaguna and María Atienza-Martínez. Technical and Energetic Assessment of a Three-Stage Thermochemical Treatment for Sewage Sludge. Energy Fuels 2013, 27, 1026−1034.

[98] Chenyu Wang YF, Ursel Hornung, Wei Zhu, Nicolaus Dahmen. Char and tar formation during hydrothermal treatment of sewage sludge in subcritical and supercritical water: Effect of organic matter composition and experiments with model compounds. Journal of Cleaner Production 242 (2020) 118586.

[99] Jacqueline M. Jarvis KOA, Justin M. Billing,Andrew J. Schmidt,Richard T. Hallen, Tanner M. Schaub. Assessment of Hydrotreatment for Hydrothermal Liquefaction Biocrudes from Sewage Sludge, Microalgae, and Pine Feedstocks. Energy Fuels 2018, 32, 8483−8493.

[100] M. Escala TZh, Ch. Koller, R. Junge, and R. Krebs. Hydrothermal Carbonization as an Energy-Efficient Alternative to Established Drying Technologies for Sewage Sludge: A Feasibility Study on a Laboratory Scale. Energy & Fuels 2013, 27, 454−460.

[101] Liping Wang YC, Aimin Li. Hydrothermal carbonization for energy-efficient processing of sewage sludge: A review. Renewable and Sustainable Energy Reviews 108 (2019) 423–440.

[102] Matteo Pecchi MB. Coupling anaerobic digestion with gasification, pyrolysis or hydrothermal carbonization: A review. Renewable and Sustainable Energy Reviews 105 (2019) 462–475.

[103] Kuo-Hsiung Lin NL, Jun-Yan Zeng, Hung-Lung Chiang. Temperature influence on product distribution and characteristics of derived residue and oil in wet sludge pyrolysis using microwave heating. Science of the Total Environment 584–585 (2017) 1248–1255.

[104] Tingting Liu ZL, Qingfu Zheng, Qianqian Lang, Yu Xia, Nana Peng, Chao Gai. Effect of hydrothermal carbonization on migration and environmental risk of heavy metals in sewage sludge during pyrolysis. Bioresource Technology 247 (2018) 282–290.

[105] Trung Ngoc Trinh PAJ, Kim Dam-Johansen,Niels Ole Knudsen, and Hanne Risbjerg Sørensen. Influence of the Pyrolysis Temperature on Sewage Sludge Product Distribution, Bio-Oil, and Char Properties. Energy & Fuels 2013, 27, 1419−1427.

[106] Jingai Shao RY, Hanping Chen, Haiping Yang, Dong Ho Lee. Catalytic effect of metal oxides on pyrolysis of sewage sludge. Fuel Processing Technology 91 (2010) 1113–1118.

[107] Ningbo Gao CQ, Baoling Liu, Zongyang Li, Chunfei Wu, and Aimin Li. Continuous pyrolysis of sewage sludge in a screw-feeding reactor: products characterization and ecological risk assessment of heavy metals. Energy & Fuels 2017, 31, 5063−5072.

[108] Eun-Seuk Park B-SK, and Joo-Sik Kim. Recovery of Oils With High Caloric Value and Low Contaminant Content By Pyrolysis of Digested and Dried Sewage Sludge Containing Polymer Flocculants. Energy & Fuels 2008, 22, 1335–1340.

[109] Isabel Fonts AJ, Gloria Gea, María B. Murillo, and Jose´L. Sanchez. Sewage Sludge Pyrolysis in Fluidized Bed, 1: Influence of Operational Conditions on the Product Distribution. Ind Eng Chem Res 2008, 47, 5376–5385.

[110] Fei Huang YY, He Huang. Temperature influence and distribution of bio-oil from pyrolysis of granular sewage sludge. Journal of Analytical and Applied Pyrolysis 130 (2018) 36–42.

[111] J. Alvarez GL, M. Amutio, M. Artetxe, I. Barbarias, A. Arregi, J. Bilbao, M. Olazar. Characterization of the bio-oil obtained by fast pyrolysis of sewage sludge in a conical spouted bed reactor. Fuel Processing Technology 149 (2016) 169–175.

[112] Renato O. Arazo DADG, Mark Daniel G. de Luna,Sergio C. Capareda. Bio-oil production from dry sewage sludge by fast pyrolysis in an electrically-heated fluidized bed reactor. Sustainable Environment Research 27 (2017) 7-14.

[113] Junwen Zhou SL, Nan Zhou, Liangliang Fan, Yaning Zhang, Peng Peng, Erik Anderson, Kuan Ding, Yunpu Wang, Yuhuan Liu, Paul Chen, Roger Ruan. Development and application of a continuous fast microwave pyrolysis system for sewage sludge utilization. Bioresource Technology 256 (2018) 295–301.

[114] I. Fonts MA, G. Gea, M.B. Murillo. Study of the pyrolysis liquids obtained from different sewage sludge. J Anal Appl Pyrolysis 85 (2009) 184–191.

[115] Guan-Bang Chen J-WL, Hsien-Tsung Lin, Fang-Hsien Wu and Yei-Chin Chao. A Study of the Production and Combustion Characteristics of Pyrolytic Oil from Sewage Sludge Using the Taguchi Method. Energies 2018, 11, 2260.

[116] Leguan Zhang BX, Zhiquan Hu, Shiming Liu, Gong Cheng, Piwen He, Lei Sun. Tar-free fuel gas production from high temperature pyrolysis of sewage sludge. Waste Management 34 (2014) 180–184.

[117] M. Inguanzo ADn, J.A. Mene´ndez, C.G. Blanco, J.J. Pis. On the pyrolysis of sewage sludge: the influence of pyrolysis conditions on solid, liquid and gas fractions. Journal of Analytical and Applied Pyrolysis 63 (2002) 209–222.

[118] Junwei Jin YL, Jianyun Zhang, Shengchun Wu, Yucheng Cao, Peng Liang,Jin Zhang, Ming Hung Wong, Minyan Wang, Shengdao Shand, Peter Christie. Influence of pyrolysis temperature on properties and environmental safety of heavy metals in biochars derived from municipal sewage sludge. Journal of Hazardous Materials 320 (2016) 417–426.

[119] K.M. Smith GDF, S. Pullket, N.J.D. Graham. Sewage sludge-based adsorbents: A review of their production, properties and use in water treatment applications. Water Research 43(2009) 2569-2594.

[120] Karin Bj€orklund LYL. Adsorption of organic stormwater pollutants onto activated carbon from sewage sludge. Journal of Environmental Management 197 (2017) 490-497.

[121] Y. Yang YQZ, A.O. Babatunde, L. Wang, Y.X. Ren, Y. Han. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. Separation and Purification Technology 51 (2006) 193–200.

[122] Panagiotis Regkouzas ED. Adsorption of selected organic micro-pollutants on sewage sludge biochar. Chemosphere 224 (2019) 840-851.

[123] Yu Jiang TD, Kai Yang, Hongyu Wang. Removal performance of phosphate from aqueous solution using a high-capacity sewage sludge-based adsorbent. Journal of the Taiwan Institute of Chemical Engineers 76 (2017) 59–64.

[124] Md Manik Mian GL, Biao Fu. Conversion of sewage sludge into environmental catalyst and microbial fuel cell electrode material: A review. Science of the Total Environment 666 (2019) 525–539.

[125] Paulina Godlewska AS, Magdalena Kończak, Patryk Oleszczuk. Adsorption capacity of phenanthrene and pyrene to engineered carbonbased adsorbents produced from sewage sludge or sewage sludge-biomass mixture in various gaseous conditions. Bioresource Technology 280 (2019) 421–429.

[126] Devon Barry CB, Cedric Briens, Franco Berruti. Pyrolysis as an economical and ecological treatment option for municipal sewage sludge. Biomass and Bioenergy 122 (2019) 472–480.

[127] Jae Hac Ko JW, Qiyong Xu. Characterization of particulate matter formed during sewage sludge pyrolysis. Fuel 224 (2018) 210–218.

[128] L.F. Calvo MO, B.M. Jenkins, A.I. Garc´ıa , A. Morán,. Heating process characteristics and kinetics of sewage sludge in different atmospheres. Thermochimica Acta 409 (2004) 127–135.

[129] Rong Han CZ, Jinwen Liu, Aixia Chen, Hongtao Wang. Thermal characterization and syngas production from the pyrolysis of biophysical dried and traditional thermal dried sewage sludge. Bioresource Technology 198 (2015) 276–282.

[130] Guangrui Liu HS, Jinhu Wua. Thermogravimetric study and kinetic analysis of dried industrial sludge pyrolysis. Waste Management 41 (2015) 128–133.

[131] Pedroza MMS, J. F.; Vieira, G. E. G.; Bezerra, M. B. D. Bio-Oil and Biogas from the Pyrolysis of Sewage Sludge, and Non-Isothermal Degradtion on USY Zeolite. Brazilian Journal of Petroleum and Gas, v 11 n 3, p 149-163, 2017, ISSN 1982-0593.

[132] Ningbo Gao JL, Benyu Qi, Aimin Li, Yue Duan, Ze Wang. Thermal analysis and products distribution of dried sewage sludge pyrolysis. Journal of Analytical and Applied Pyrolysis 105 (2014) 43–48.

[133] A. Soria-Verdugo NG-H, L.M. Garcia-Gutierrez, U. Ruiz-Rivas. Analysis of biomass and sewage sludge devolatilization using the distributed activation energy model. Energy Conversion and Management 65 (2013) 239–244.

[134] Wang Xiaohuaa JJ. Effect of Heating Rate on the Municipal Sewage Sludge Pyrolysis Character. Energy Procedia 14 (2012) 1648-1652.

[135] Aimin Ji SZ, Xuebin Lu, Yong Liu. A new method for evaluating the sewage sludge pyrolysis kinetics. Waste Management 30 (2010) 1225–1229.

[136] Salman Raza Naqvi RT, Zeeshan Hameed, Imtiaz Ali, Muhammad Naqvi, Wei-Hsin Chen, Selim Ceylan, Harith Rashid, Junaid Ahmad, Syed A. Taqvi, Muhammad Shahbaz. Pyrolysis of high ash sewage sludge: Kinetics and thermodynamic analysis using Coats-Redfern method. Renewable Energy 131 (2019) 854-860.

[137] M.B. Folgueras RMD. Influence of FeCl3 and lime added to sludge on sludgeecoal pyrolysis. Energy 35 (2010) 5250-5259.

[138] Jon Alvarez MA, Gartzen Lopez, Javier Bilbao, Martin Olazar. Fast co-pyrolysis of sewage sludge and lignocellulosic biomass in a conical spouted bed reactor. Fuel 159 (2015) 810–818.

[139] Antonio Soria-Verdugo EG, Andrés Morato-Godino, Nestor García-Hernando, Uwe Riedel. Pyrolysis of biofuels of the future: Sewage sludge and microalgae – Thermogravimetric analysis and modelling of the pyrolysis under different temperature conditions. Energy Conversion and Management 138 (2017) 261–272.

[140] Jinjiao Zhu YY, Li Yang, Yuezhao Zhu. High quality syngas produced from the copyrolysis of wet sewage sludge with sawdust. Interntional Journal of Hydrogen Energy 43 (2018) 5463-5472.

[141] Hua-jun Huang TY, Fa-ying Lai, Guo-qiang Wu. Co-pyrolysis of sewage sludge and sawdust/rice straw for the production of biochar. Journal of Analytical and Applied Pyrolysis 125 (2017) 61–68.

[142] Yu-Fong Huang C-HS, Pei-Te Chiueh, Shang-Lien Lo. Microwave co-pyrolysis of sewage sludge and rice straw. Energy 87 (2015) 638-644.

[143] Salman Raza Naqvi ZH, Rumaisa Tariq, Syed A. Taqvi, Imtiaz Ali, M. Bilal Khan Niazi, Tayyaba Noor, Arshad Hussain, Naseem Iqbal, M. Shahbaz. Synergistic effect on co-pyrolysis of rice husk and sewage sludge by thermal behavior, kinetics, thermodynamic parameters and artificial neural network. Waste Management 85 (2019) 131–140.

[144] Xuebin Wang SD, Houzhang Tan, Adewale Adeosun, Milan Vujanovic, Fuxin Yang,Neven Duic. Synergetic effect of sewage sludge and biomass co-pyrolysis: A combined study in thermogravimetric analyzer and a fixed bed reactor. Energy Conversion and Management 118 (2016) 399–40.

[145] Junwei Jin MW, Yucheng Cao, Shengchun Wu, Peng Liang, Yanan Li, Jianyun Zhang, Jin Zhang, Ming Hung Wong, Shengdao Shan, Peter Christie. Cumulative effects of bamboo sawdust addition on pyrolysis of sewage sludge: Biochar properties and environmental risk from metals. Bioresource Technology 228 (2017) 218–226.

[146] Nadia Ruiz-Gómez VQ, Javier Ábrego, María Atienza-Martínez, María Benita Murillo, Gloria Gea. Co-pyrolysis of sewage sludge and manure. Waste Management 59 (2017) 211–221.

[147] Bing Zhao XX, Haibo Li, Xi Chen, Fanqiang Zeng. Kinetics evaluation and thermal decomposition characteristics of copyrolysis of municipal sewage sludge and hazelnut shell. Bioresource Technology 247 (2018) 21–29.

[148] Zhipu Wang KL, Like Xie, Henan Zhu, Shibo Ji, Xinqian Shu. Effects of residence time on characteristics of biochars prepared via copyrolysis of sewage sludge and cotton stalks. Journal of Analytical and Applied Pyrolysis 142 (2019) 104659.

[149] Yan Lin YL, Zhaosheng Yu, Shiwen Fang, Yousheng Lin, Yunlong Fan, Xiaowei Peng, Xiaoqian Ma. Co-pyrolysis kinetics of sewage sludge and oil shale thermal decomposition using TGA–FTIR analysis. Energy Conversion and Management 118 (2016) 345–352.

[150] Xiao Yang CY, Jiao Xu, Weijiang Zhang. Potential method for gas production: High temperature co-pyrolysis of lignite and sewage sludge with vacuum reactor and long contact time. Bioresource Technology 179 (2015) 602–605.

[151] Yan Lin YL, Zhaosheng Yu, Shiwen Fang, Xiaoqian Ma. A study on co-pyrolysis of bagasse and sewage sludge using TG-FTIR and Py- GC/MS. Energy Conversion and Management 151 (2017) 190–198.

[152] Qindong Chen HL, JaeHac Ko, Huanan Wu, Qiyong Xu. Structure characteristics of bio-char generated from co-pyrolysis of wooden waste and wet municipal sewage sludge. Fuel Processing Technology 183 (2019) 48–54.

[153] Guanyi Chen RY, Zhanjun Cheng, Beibei Yan, Wenchao Ma. Nitric oxide formation during corn straw/sewage sludge co-pyrolysis/ gasification. Journal of Cleaner Production 197 (2018) 97e105.

[154] Fu-Jun Tian B-QL, Yong Chen, Chun-Zhu Li. Formation of NOx precursors during the pyrolysis of coal and biomass. Part V. Pyrolysis of a sewage sludge. Fuel 81 (2002) 2203–2208.

[155] M. Bele´n Folgueras RMaDa, Jorge Xiberta. Pyrolysis of blends of different types of sewage sludge with one bituminous coal. Energy 30 (2005) 1079–1091.

[156] Juan Li XX, Jiao Li, Mei Shi, Aijun Lin, Congbin Xu, Jianzhong Zheng, Ronghua Li. Preparation of thiol-functionalized activated carbon from sewage sludge with coal blending for heavy metal removal from contaminated water. Environmental Pollution 234 (2018) 677-683.

[157] Jing-Pei Cao PS, Xiao-Yan Zhao, Xian-YongWei, Takayuki Takarad. Catalytic reforming of volatiles and nitrogen compounds from sewage sludge pyrolysis to clean hydrogen and synthetic gas over a nickel catalyst. Fuel Processing Technology 123 (2014) 34–40.

[158] Yanjun Hu WY, Haryo Wibowo, Yuanyuan Xia, Yanjun Lu, Mi Yan. Effect of catalysts on distribution of polycyclic-aromatic hydrocarbon (PAHs) in bio-oils from the pyrolysis of dewatered sewage sludge at high and low temperatures. Science of the Total Environment 667 (2019) 263–270.

[159] Hyun Ju Park HSH, Young-Kwon Park, Jin-Heong Yim, Jong-Ki Jeon, Junhong Park, Changkook Ryu, Seung-Soo Kim. Clean bio-oil production from fast pyrolysis of sewage sludge: Effects of reaction conditions and metal oxide catalysts. Bioresource Technology 101 (2010) S83–S85.

[160] Siqi Tang FY, Chunmiao Zheng,and Zuotai Zhang. Novel Calcium Oxide-Enhancement Phosphorus Recycling Technique through Sewage Sludge Pyrolysis. Chem Eng 2018, 6, 9167−9177.

[161] Kaige Wang YZ, Xifeng Zhu, Catherine E. Brewer, Robert C. Brown. Ex-situ catalytic pyrolysis of wastewater sewage sludge – A micropyrolysis study. Bioresource Technology 232 (2017) 229–234.

[162] Guangyi Liu MMW, Qingliang Zhao, and Robert C. Brown. Hydrocarbon and Ammonia Production from Catalytic Pyrolysis of Sewage Sludge with Acid Pretreatment. ACS Sustainable Chem Eng 2016, 4, 1819−1826.

[163] Ke Tian W-JL, Ting-Ting Qian, Hong Jiang, and Han-Qing Yu. Investigation on the Evolution of NContaining Organic Compounds during Pyrolysis of Sewage Sludge. Environ Sci Technol 2014, 48, 10888−10896.

[164] Qinglong Xie PP, Shiyu Liu, Min Min, Yanling Cheng, Yiqin Wana, Yun Li, Xiangyang Lin, Yuhuan Liu, Paul Chen, Roger Ruan. Fast microwave-assisted catalytic pyrolysis of sewage sludge for bio-oil production. Bioresource Technology 172 (2014) 162–168.

[165] Bo Gu J-PC, Fu Wei, Xiao-Yan Zhao, Xue-Yu Ren, Chen Zhu, Zhen-Xing Guo, Jin Bai, Wen-Zhong Shen, Xian-Yong Wei. Nitrogen migration mechanism and formation of aromatics during catalytic fast pyrolysis of sewage sludge over metal-loaded HZSM-5. Fuel 244 (2019) 151–158.

[166] Guotao Yu YF, Dezhen Chen, Min Yang,Tianchi Yu and Xiaohu Dai. In Situ Reforming of the Volatile by Char during Sewage Sludge Pyrolysis. Energy Fuels 2016, 30, 10396−10403.

[167] Pornlada Daorattanachai WL, Apirat Laobuthee, Navadol Laosiripojan. Type of contribution: Research article catalytic activity of sewage sludge char supported Re-Ni bimetallic catalyst toward cracking/reforming of biomass tar. Renewable Energy 121 (2018) 644-651.

[168] Yuting Tu ST, Lingjun Kong, Ya Xiong. Co-catalytic effect of sewage sludge-derived char as the support of Fenton-like catalyst. Chemical Engineering Journal 185– 186 (2012) 44– 51.

[169] Andrew Ng Kay Lup FA, Wan Mohd Ashri Wan Daud, Mohamed Kheireddine Aroua. A review on reactivity and stability of heterogeneous metal catalysts for deoxygenation of bio-oil model compounds. Journal of Industrial and Engineering Chemistry 56 (2017) 1–34.

[170] Guotao Yu DC, Umberto Arena, Zhen Huang, Xiaohu Dai. Reforming sewage sludge pyrolysis volatile with Fe-embedded char: Minimization of liquid product yield. Waste Management 73 (2018) 464–475.

[171] M. Azuara IFb, F. Bimbela, M.B.Murillo, G. Gea. Catalytic post-treatment of the vapors from sewage sludge pyrolysis by means of γ-Al2O3: Effect on the liquid product properties. Fuel Processing Technology 130 (2015) 252–262.

[172] Yu Sun BJ, Wei Wu, Wu Zuo, Ya Zhang, Yong Zhang, Yaji Huang. Effects of temperature and composite alumina on pyrolysis of sewage sludge. Journal of Envirnmental Sciences 30 (2015) 1-8

[173] Huan Liu QZ, Haoxuan Xing, Hongyun Hu, Aijun Li, Hong Yao. Product distribution and sulfur behavior in sewage sludge pyrolysis: Synergistic effect of Fenton peroxidation and CaO conditioning. Fuel 159 (2015) 68–75.

[174] Jian Song JY, Sha Liang, Yafei Shi, Wenbo Yu, Chao Li, Xinyu Xu, Jun Xiao, Ruonan Guan, Nan Ye, XuWu, Huijie Hou, Jingping Hu, Jiukun Hu, Bo Xiao. Red mud enhanced hydrogen production from pyrolysis of deep-dewatered sludge cakes conditioned with Fenton's reagent and red mud. International Journal of Hydrogen Energy 41(2016) 16762-16771.

[175] Fu Wei J-PC, Xiao-Yan Zhao, Jie Ren, Bo Gu, Xian-Yong Wei. Formation of aromatics and removal of nitrogen in catalytic fast pyrolysis of sewage sludge: A study of sewage sludge and model amino acids. Fuel 218 (2018) 148–154.

[176] Y. Kim WP. A technical and economic evaluation of the pyrolysis of sewage sludge for the production of bio-oil. Bioresource Technology 99 (2008) 1409–1416.

[177] Hui Chen DC, Liu Hong. Influences of activation agent impregnated sewage sludge pyrolysis on emission characteristics of volatile combustion and De-NOx performance of activated char. Applied Energy 156 (2015) 767–775.

[178] J. A. Garcia-Nunez MRP-S, M. E. Garcia-Perez,I. Fonts,J. Abrego,R. J. M. Westerhofand M. Garcia-Perez. Historical Developments of Pyrolysis Reactors: A Review. Energy Fuels 2017, 31, 5751−5775.

[179] M. Azuara IF, P. Barcelona, M.B. Murillo, G. Gea. Study of catalytic post-treatment of the vapours from sewage sludge pyrolysis by means of Al2O3. Fuel 107 (2013) 113–121.

[180] Wu Zuo BJ, Yaji Huang, Yu Sun, Rui Li, Jiqiang Jia. Pyrolysis of high-ash sewage sludge in a circulating fluidized bed reactor for production of liquids rich in heterocyclic nitrogenated compounds. Bioresource Technology 127 (2013) 44–48.

[181] Chunmei Ran YL, Azka Rizwana Siddiqui, Asif Ali Siyal, Xiao Mao, Qinhao Kang, Jie Fu, Wenya Ao, Jianjun Dai. Pyrolysis of textile dyeing sludge in fluidized bed and microwave assisted auger reactor: Comparison, migration and distribution of heavy metals. Energy 182 (2019) 337-348.

[182] Yang Liu CR, Azka Rizwana Siddiqui, Xiao Mao, Qinhao Kang, Jie Fu, Zeyu Deng, Yongmeng Song, Zhihui Jiang, Tianhao Zhang, Jianjun Dai. Pyrolysis of textile dyeing sludge in fluidized bed and microwave-assisted auger reactor: Comparison and characterization of pyrolysis products. Journal of Hazardous Materials 359 (2018) 454–464.

[183] C. Karaca SS, D. Orhon, H. Okutan. High temperature pyrolysis of sewage sludge as a sustainable process for energy recovery. Waste Management 78 (2018) 217–226.

[184] Siyi Luo YF. The production of hydrogen-rich gas by wet sludge pyrolysis using waste heat from blast-furnace slag. Energy 113 (2016) 845-851.

[185] M. Atienza-Martínez IR, I. Fonts, J. Ceamanos a, G. Gea. Effect of torrefaction on the catalytic post-treatment of sewage sludge pyrolysis vapors using c-Al2O3. Chemical Engineering Journal 308 (2017) 264–274.

[186] Zuopeng Gao HZ, Wenya Ao, Jing Li, Guangqing Liu, Xiaochun Chen, Jie Fu, Chunmei Ran, Yang Liu, Qinhao Kang, Xiao Mao, Jianjun Dai. Microwave pyrolysis of textile dyeing sludge in a continuously operated auger reactor: Condensates and non-condensable gases. Environmental Pollution 228 (2017) 331-343.

[187] Vargas TLSLG. Models, Methods, Concepts & Applications of the Analytic Hierarchy Process.Second Edition.

[188] Saaty TL. Decision making with the analytic hierarchy process.Int. J. Services Sciences, Vol. 1, No. 1, 2008.

[189] Elanur Adar BK, Mahir İnce, Mehmet Sinan Bilgili. Comparison of methods for sustainable energy management with sewage sludge in Turkey based on SWOT-FAHP analysis. Renewable and Sustainable Energy Reviews 62 (2016) 429–440.

[190] Jumoke Oladejo KS, Xiang Luo, Gang Yang and Tao Wu. A Review of Sludge-to-Energy Recovery Methods. Energies 2019, 12, 60.

[191] Vineet Singh Sikarwara MZ, Paul S. Fennell,Nilay Shah,Edward J.Anthony. Progress in biofuel production from gasification. Progress in Energy and Combustion Science 61 (2017) 189-248.

[192] Vineet Singh Sikarwara MZ, Peter Cloughd, Joseph Yaod, Xia Zhonge, Mohammad Zaki Memona, Nilay Shahd, Edward J. Anthony and Paul S. Fennell. An overview of advances in biomass gasification. Energy & Environmental Science 2016, 9, 2939-2977.

[193] Vineet S. Sikarwar GJ, Ming Zhao and Yujue Wang. Equilibrium Modeling of Sorption-Enhanced Cogasification of Sewage Sludge and Wood for Hydrogen-Rich Gas Production with in Situ Carbon Dioxide Capture. Ind Eng Chem Res 2017, 56, 5993−6001.

[194] Smoliński BUaA. Kinetics of Sewage Sludge Pyrolysis and Air Gasification of Its Chars. Energy Fuels 2016, 30, 4869−4878.

[195] Lech Nowicki MM. Gasification of pyrolysis chars from sewage sludge. Fuel 143 (2015) 476–483.

[196] Xie Li-ping LT, Gao Jian-dong, Fei Xue-ning, Wu Xia, Jiang Yuan-guang. Effect of moisture content in sewage sludge on air gasification. Fuel Chem Technol, 2010, 38(5), 615-620.

[197] Susanna Nilsson AG-B, Diego Fuentes Cano. Gasification reactivity of char from dried sewage sludge in a fluidized bed. Fuel 92 (2012) 346–353.

[198] Werle S. Gasification of a Dried Sewage Sludge in a Laboratory Scale Fixed Bed Reactor. Energies 2015, 8, 8562-8572.

[199] Nimit Nipattummakul IIA, Somrat Kerdsuwan, Ashwani K. Gupta. Hydrogen and syngas production from sewage sludge via steam gasification. International Journal of Energy 35 (2010) 11738-11745.

[200] Jian-guo Zhu YY, Qing-gang Lu, Ming Gao, Zi-qu Ouyang. Experimental investigation of gasification and incineration characteristics of dried sewage sludge in a circulating fluidized bed. Fuel 150 (2015) 441–447.

[201] Manuel Campoy AG-B, Pedro Ollero, Susanna Nilsson. Gasification of wastes in a pilot fluidized bed gasifier. Fuel Processing Technology 121 (2014) 63–69.

[202] Tobias Pape Thomsen ZS, Benny Gøbel, Peder Stoholm, Jesper Ahrenfeldt, Flemming Jappe Frandsen, Ulrik Birk Henriksen. Low temperature circulating fluidized bed gasification and co-gasification of municipal sewage sludge. Part 1: Process performance and gas product characterization. Waste Management 66 (2017) 123–133.

[203] I. Petersen JW. Experimental investigation and modeling of gasification of sewage sludge in the circulating fluidized bed. Chemical Engineering and Processing 44 (2005) 717–736.

[204] I. Petersen JW. Three-dimensional modeling of a circulating fluidized bed gasifier for sewage sludge. Chemical Engineering Science 60 (2005) 4469 – 4484.

[205] Cesare Freda GC, Assunta Romanelli, Vito Valerio, Massimiliano Grieco. Sewage sludge gasification in a bench scale rotary kiln. Fuel 212 (2018) 88–94.

[206] Nerijus Striugas VV, Nerijus Pedišius, Robertas Poškas, Kestutis Zakarauskas. Investigation of sewage sludge treatment using air plasma assisted gasification. Waste Management 64 (2017) 149–160.

[207] A. Mountouris EV, D. Tassios. Plasma gasification of sewage sludge: Process development and energy optimization. Energy Conversion and Management 49 (2008) 2264–2271.

[208] Felicia Fock UH, Niels Houbakb, Kirstine P. B. Thomsenc. Demonstration of the Vortex Process for biomass gasifiers. 12th European Biomass Conference - Amsterdam, Netherlands (2002) 670-676.

[209] M. A. Elliott HP. Gasification of Pulverized Coal with Oxygen and Steam in a Vortex Reactor. Industrial and Engneering Chemistry Vol 44, No 5.

[210] Young-Kon Choi J-HK, Joo-Sik Kim. A new type three-stage gasification of dried sewage sludge: Effects of equivalence ratio, weight ratio of activated carbon to feed, and feed rate on gas composition and tar, NH3, and H2S removal and results of approximately 5h gasification. Energy 118 (2017) 139-146.

[211] M. Seggiani SV, M. Puccini, A. Bellini. Cogasification of sewage sludge in an updraft gasifier. Fuel 93 (2012) 486–491.

[212] Weerachai Arjharn TH, Pansa Liplap, and G. S. Vijaya Raghavan. Evaluation of an Energy Production System from Sewage Sludge Using a Pilot-Scale Downdraft Gasifier. Energy Fuels 2013, 27, 229−236.

[213] Jamison Watson YZ, Buchun Si, Wan-Ting Chen, Raquel de Souza. Gasification of biowaste: A critical review and outlooks. Renewable and Sustainable Energy Reviews 83 (2018) 1–17.

[214] Uisung Lee JD, J.N. Chung. Experimental investigation of sewage sludge solid waste conversion to syngas using high temperature steam gasification. Energy Conversion and Management 158 (2018) 430–436.

[215] Y.W. Huang MQC, Q.H. Li, W. Xing. Hydrogen-rich syngas produced from co-gasification of wet sewage sludge and torrefied biomass in self-generated steam agent. Energy 161 (2018) 202-213.

[216] N. Gil-Lalaguna JLS, M.B. Murillo, E. Rodríguez, G. Gea. Air–steam gasification of sewage sludge in a fluidized bed. Influence of some operating conditions. Chemical Engineering Journal 248 (2014) 373–382.

[217] N. Gil-Lalaguna JLS, M.B. Murillo, V. Ruiz, G. Gea. Air-steam gasification of char derived from sewage sludge pyrolysis. Comparison with the gasification of sewage sludge. Fuel 129 (2014) 147–155.

[218] Chao Gai MC, Tingting Liu, Nana Peng, Zhengang Liu. Gasification characteristics of hydrochar and pyrochar derived from sewage sludge. Energy 113 (2016) 957-965.

[219] Adnan Midilli MD, Colin R. Howarth, Mike J. Ling, Teoman Ayhan. Combustible gas production from sewage sludge with a downdraft gasifier. Energy Conversion & Management 42 (2001) 157-172.

[220] Kung-Yuh Chiang C-HL, Chun-Kai Liao, Ray Hsien-Ruen Ger Characteristics of hydrogen energy yield by co-gasified of sewage sludge and paper-mill sludge in a commercial scale plant. International Joournal of Hydrogen Energy 41 (2016) 21641-21648.

[221] Maurizia Seggiani MP, Giovanni Raggio, Sandra Vitolo. Effect of sewage sludge content on gas quality and solid residues produced by cogasification in an updraft gasifier. Waste Management 32 (2012) 1826–1834.

[222] Lixin Peng YW, Zhihong Lei, Gong Cheng. Co-gasification of wet sewage sludge and forestry waste in situ steam agent. Bioresource Technology 114 (2012) 698–702.

[223] G. García JA, A.Gonzalo, J.L.Sánchez, J.Ábrego. Influence of feedstock composition in fluidised bed co-gasification of mixtures of lignite,bituminous coal and sewage sludge. Chemical Engineering Journal 222 (2013) 345–352.

[224] Jing Ma MC, Tianxue Yang, Zhengang Liu, Wentao Jiao, Dong Li, Chao Gai. Gasification performance of the hydrochar derived from co-hydrothermal carbonization of sewage sludge and sawdust. Energy 173 (2019) 732-739.

[225] K. Gorazda BT, S. Werle, Z. Wzorek. Sewage sludge as a fuel and raw material for phosphorus recovery: Combined process of gasification and P extraction. Waste Management 73 (2018) 404–415.
[226] Adam Smolinski NH. Co-gasification of coal/sewage sludge blends to hydrogen-rich gas with the application of simulated high temperature reactor excess heat. International Journal of Hydrogen Energy 41 (2016) 8154-8158.
[227] Daniel Schwitalla MR, Clemens Forman, Christian Wolfersdorf, Matthias Gootz, Jin Bai, Stefan Guhl, Markus Neuroth, Bernd Meyer. Ash and slag properties for co-gasification of sewage sludge and coal: An experimentally validated modeling approach. Fuel Processing Technology 175 (2018) 1–9.
[228] Filomena Pinto RNA, Helena Lopes, Ma´rio Dias, I. Gulyurtlu, and I. Cabrita. Effect of Experimental Conditions on Gas Quality and Solids Produced by Sewage Sludge Cogasification. 2. Sewage Sludge Mixed with Biomass. Energy & Fuels 2008, 22, 2314–2325.
[229] Tobias Pape Thomsen HH-N, Benny Gøbel, Peder Stoholm, Jesper Ahrenfeldt, Ulrik B. Henriksen, Dorette Sophie Müller-Stöver. Low temperature circulating fluidized bed gasification and co-gasification of municipal sewage sludge. Part 2: Evaluation of ash materials as phosphorus fertilizer. Waste Management 66 (2017) 145–154.
[230] Tae-Young Mun J-WK, Joo-Sik Kim. Air gasification of dried sewage sludge in a two-stage gasifier: Part 1. The effects and reusability of additives on the removal of tar and hydrogen production. International Journal of Hydrogen Energy 3 8 (2013) 5226-5234.
[231] Elena Roche JMdA, Adolfo Narros, María Encarnación Rodríguez. Air and air-steam gasification of sewage sludge. The influence of dolomite and throughput in tar production and composition. Fuel 115 (2014) 54–61.
[232] Siming You YSO, Season S. Chen, Daniel C.W. Tsang, Eilhann E. Kwon, Jechan Lee,Chi-Hwa Wang. A critical review on sustainable biochar system through gasification: Energy and environmental applications. Bioresource Technology 246 (2017) 242–253.
[233] Jing-Pei Cao XH, Xiao-Yan Zhao, Ben-Shui Wang, Sirimirin Meesuk, Kazuyoshi Sato, Xian-Yong Wei, Takayuki Takarad. Low-temperature catalytic gasification of sewage sludge-derived volatiles to produce clean H2-rich syngas over a nickel loaded on lignite char. International Journal of Hydrogen Energy 39 (2014) 9193-9199.
[234] Geng Lu HL, Qiang Zhang, Jiaxing Wang, Linlin Yi, Hongyun Hu, Hong Yao. Nitrogen conversion during the homogeneous and heterogeneous stages of sludge steam gasification: Synergistic effects of Fenton's reagent and CaO conditioner. Fuel 241 (2019) 1109–1116.
[235] M. Schmid MB, D. Schweitzer, G. Waizmann, R. Spörl, G. Scheffknecht. Product gas composition for steam-oxygen fluidized bed gasification of dried sewage sludge, straw pellets and wood pellets and the influence of limestone as bed material. Biomass and Bioenergy 117 (2018) 71–77.
[236] Huan Liu HH, Guangqian Luo, Aijun Li, Minghou Xu, Hong Yao. Enhancement of hydrogen production in steam gasification of sewage sludge by reusing the calcium in lime-conditioned sludge. International Journal of Hydrogen Energy 38 (2013) 1332-1341.
[237] Xiaoxia Yang ST, Tao Kan, Yuxiang Zhu, Honghui Xu, Vladimir Strezov, Peter Nelson, Yijiao Jiang. Sorption-enhanced thermochemical conversion of sewage sludge to syngas with intensified carbon utilization. Applied Energy 254 (2019) 113663.

[238] Young-Kon Choi M-HC, Joo-Sik Kim. Air gasification of dried sewage sludge in a two-stage gasifier. Part 4: Application of additives including Ni-impregnated activated carbon for the production of a tar-free and H2-rich producer gas with a low NH3 content. International Journal of Hydrogen Energy 41 (2016) 1460-1467.

[239] Juan Manuel de Andrés AN, María Encarnación Rodríguez. Air-steam gasification of sewage sludge in a bubbling bed reactor: Effect of alumina as a primary catalyst. Fuel Processing Technology 92 (2011) 433–440.

[240] Tae-Young Mun J-SK. Air gasification of dried sewage sludge in a two-stage gasifier. Part 2: Calcined dolomite as a bed material and effect of moisture content of dried sewage sludge for the hydrogen production and tar removal. International Journal of Hydrogen Energy 38 (2013) 5233-5242.

[241] Juan Manuel de Andrés ER, Adolfo Narros, María Encarnación Rodríguez. Characterisation of tar from sewage sludge gasification. Influence of gasifying conditions: Temperature, throughput, steam and use of primary catalysts. Fuel 180 (2016) 116–126.

[242] Shiyi Chen ZS, Qi Zhang, Jun Hu, Wenguo Xiang. Steam gasification of sewage sludge with CaO as CO2 sorbent for hydrogen-rich syngas production. Biomass and Bioenergy 107 (2017) 52-62.

[243] Mian Hu LG, Zhihua Chen, Caifeng Ma, Yan Zhou, Jian Chen, Shu Ma, Mahmood Laghari, Bo Xiao, Beiping Zhang, Dabin Guo. Syngas production by catalytic in-situ steam co-gasification of wet sewage sludge and pine sawdust. Energy Conversion and Management 111 (2016) 409–416.

[244] Qiwu Zhang JK. A new approach for hydrogen generation from sewage sludge. Bioresource Technology 201 (2016) 191–194.

[245] Huan Liu LY, Qiang Zhang, Hongyun Hu, Geng Lu, Aijun Li, Hong Yao. Co-production of clean syngas and ash adsorbent during sewage sludge gasification: Synergistic effect of Fenton peroxidation and CaO conditioning. Applied Energy 179 (2016) 1062–1068.

[246] Young-Kon Choi M-HC, Joo-Sik Kim. Steam/oxygen gasification of dried sewage sludge in a two-stage gasifier: Effects of the steam to fuel ratio and ash of the activated carbon on the production of hydrogen and tar removal. Energy 91 (2015) 160-167.

[247] Tae-Young Mun M-HC, Joo-Sik Kim. Air gasification of dried sewage sludge in a twostage gasifier. Part 3: Application of olivine as a bed material and nickel coated distributor for the production of a clean hydrogen-rich producer gas. International Journal of Hydrogen Energy 39 (2014) 5634-5643

[248] Guanyi Chen FL, Xiang Guo, Yanru Zhang, Beibei Yan, Zhanjun Cheng, Lin Xiao, Wenchao Ma,and Li’an Hou. Co-gasification of Acid Hydrolysis Residues and Sewage Sludge in a Downdraft Fixed Gasifier with CaO as an In-Bed Additive. Energy Fuels 2018, 32, 5893−5900.

[249] G. García EC, I. Fonts,J. L. Sánchez, and J. Herguido. Gas Catalytic Upgrading in a Two-Zone Fluidized Bed Reactor Coupled to a Cogasification Plant. Energy Fuels 2013, 27, 2835−2845.

[250] Yong-Seong Jeong Y-KC, Ki-Bum Park, Joo-Sik Kim. Air co-gasification of coal and dried sewage sludge in a two-stage gasifier: Effect of blending ratio on the producer gas composition and tar removal. Energy 185 (2019) 708-71.

[251] Johannes W. Judex MG, H. Christian Burgbacher. Gasification of dried sewage sludge: Status of the demonstration and the pilot plant. Waste Management 32 (2012) 719–723.

[252] Azize Ayol OTY, Alim Gurgen. Investigation of municipal sludge gasification potential: Gasification characteristics of dried sludge in a pilot-scale downdraft fixed bed gasifier. International Journal of Hydrogen Energy 44(2019) 17397-17410.

[253] Daniel Schweitzer AG, Max Schmid, Gebhard Waizmann, Marcel Beirow, Reinhold Sporl, Günter Scheffknecht. Steam gasification of wood pellets, sewage sludge and manure: Gasification performance and concentration of impurities. Biomass and Bioenergy 111 (2018) 308-319.

[254] Takahashi H. Study on sewage sludge gasficiation. Bureau of Sewerage, Tokyo Metropolitan Government

[255] Center. GGT. Technology Assessment Report. EPA/600/R-12/540 June 2012 Version 15.

[256] Osamu Sawai TN, Kazuo Yamamoto. Supercritical water gasification of sewage sludge using bench-scale batch reactor: advantages and drawbacks. J Mater Cycles Waste Manag (2014) 16:82–92.

[257] Nancy Y. Acelas DPL, D.W.F. (Wim) Brilman, Sascha R.A. Kersten, A. Maarten J. Kootstra. Supercritical water gasification of sewage sludge: Gas production and phosphorus recovery. Bioresource Technology 174 (2014) 167–175.

[258] Takahiro Murakami YS, Hidekazu Nagasawa, Takafumi Yamamoto, Takami Koseki, Hitoshi Hirose, Seiichiro Okamoto. Combustion characteristics of sewage sludge in an incineration plant for energy recovery. Fuel Processing Technology 90 (2009) 778–783.

[259] Bartłomiej Michał Cieslik JN, Piotr Konieczka. Review of sewage sludge management: standards, regulations and analytical methods. Journal of Cleaner Production 90 (2015) 1-15.

[260] J. Werther TO. Sewage sludge combustion. Progress in Energy and Combustion Science 25 (1999) 55–116.

[261] Jin-Ho Sung S-KB, Bup-Mook Jeong, Jeong-Hun Kim, Hang Seok Choi, Ha-Na Jang, Yong-Chil Seo. Oxy-fuel co-combustion of sewage sludge and wood pellets with flue gas recirculation in a circulating fluidized bed. Fuel Processing Technology 172 (2018) 79–85.

[262] M. SaÈnger JW, T. Ogada. NOx and N2O emission characteristics from fluidised bed combustion of semi-dried municipal sewage sludge. Fuel 80 (2001) 167-177.

[263] Anna-Lena Elled L-EA, Bo Leckner, Bengt-Ake Andersson. The fate of trace elements in fluidised bed combustion of sewage sludge and wood. Fuel 86 (2007) 843–852.

[264] Aysegül Abusoglu EO, A.Ihsan Kutlar, Hameed Aljaf. Life cycle assessment (LCA) of digested sewage sludge incineration for heat and power production. Journal of Cleaner Production 142 (2017) 1684-1692.

[265] Dong Ho Lee RY, Jingai Shao, and David Tee Liang. Combustion Characteristics of Sewage Sludge in a Bench-Scale Fluidized Bed Reactor. Energy & Fuels 2008, 22, 2–8.

[266] Gang Zhang JH, Jiang Cheng, Zhiqi Cai, Mingzhong Ren, Sukun Zhang, Jieru Zhang. Evaluation of PCDD/Fs and metals emission from a circulating fluidized bed incinerator co-combusting sewage sludge with coal. Journal of Environmental Sciences 2013, 25(1) 231–235.

[267] Jung Min Park SBL, Jin Pil Kim, Min Jung Kim, Oh Sang Kwon, Dong Il Jung. Behavior of PAHs from sewage sludge incinerators in Korea. Waste Management 29 (2009) 690–695.

[268] Ping Fang ZT, Xiang Xiao, Jianhang Huang, Xiongbo Chen, Peiyi Zhong, Zhixiong Tang, Chaoping Cen. Using sewage sludge as a flue gas denitration agent for the cement industry: Factor assessment and feasibility. Journal of Cleaner Production 224 (2019) 292-303.

[269] Zhenzhou Yang YZ, Lili Liu, Xidong Wang, Zuotai Zhang. Environmental investigation on co-combustion of sewage sludge and coal gangue: SO2, NOx and trace elements emissions. Waste Management 50 (2016) 213–221.

[270] Xin Niu LS, Haiming Gu, Shouxi Jiang, Jun Xiao. Characteristics of hematite and fly ash during chemical looping combustion of sewage sludge. Chemical Engineering Journal 268 (2015) 236–244.

[271] Zhiqiang Wang CH, Yi Xing, Yifei Li, Lihui Feng, Mengmeng Jia. Combustion behaviors and kinetics of sewage sludge blended with pulverized coal: With and without catalysts. Waste Management 74 (2018) 288–296.

[272] Robertas Poškas AS, Hussam Jouhara, Povilas Poškas. Investigation of characteristics of solid particles from a mixture of sewage sludge and wood pellets synthetic gas and their clean-up. Waste Management 78 (2018) 1–7.

[273] A.I. Calvo LACT, E.R. Teixeira, C. Alves, T. Nunes, M. Duarte, E. Coz, D. Custodio, A. Castro, B. Artiñano, R. Fraile. Particulate emissions from the co-combustion of forest biomass and sewage sludge in a bubbling fluidised bed reactor. Fuel Processing Technology 114 (2013) 58–68.

[274] Emília Hroncová JL, Juraj Musil. Problematic issues of air protection during thermal processes related to the energetic uses of sewage sludge and other waste. Case study: Co-combustion in peaking power plant. Waste Management 73 (2018) 574–580.

[275] Rajesh Kumar RIS. An investigation of co-combustion municipal sewage sludge with biomass in a 20 kW BFB combustor under air-fired and oxygen-enriched condition. Waste Management 70 (2017) 114–126.

[276] Luciane Batistella VS, Renato C. Suzin, Elaine Virmond, Chrtistine A. Althoff,Regina F.P.M. Moreira, Humberto J. José. Gaseous emissions from sewage sludge combustion in a moving bed combustor. Waste Management 46 (2015) 430–439.

[277] Qiang Zhang HL, Xiuju Zhang, Haoxuan Xing, Hongyun Hu, Hong Yao. Novel utilization of conditioner CaO for gas pollutants control during co-combustion of sludge and coal. Fuel 206 (2017) 541–545.

[278] Rundong Li WT, Yanlong Li, Weiyun Wang, Ruoqi Cui, Tianhua Yang. Potential recovery of phosphorus during the fluidized bed incineration of sewage sludge. Journal of Cleaner Production 140 (2017) 964-970.

[279] Deng Wenyi YJ, Li Xiaodong, Wang Fei, Chi Yong, LU Shengyong. Emission characteristics of dioxins, furans and polycyclic aromatic hydrocarbons during fluidized-bed combustion of sewage sludge. Journal of Environmental Sciences 21(2009) 1747–1752.

[280] Jingyong Liu JZ, Shuiyu Sun, Shaosong Huang, Jiahong Kuo, Nanwei Chen. Combined effects of FeCl3 and CaO conditioning on SO2, HCl and heavy metals emissions during the DDSS incineration. Chemical Engineering Journal 299 (2016) 449–458.

[281] Yuyan Huang HL, Zhengwu Jiang, Xiaojie Yang, Qing Chen. Migration and transformation of sulfur in the municipal sewage sludge during disposal in cement kiln. Waste Management 77 (2018) 537–544.

[282] W.D. Chanaka Udayanga AV, Apostolos Giannis, Grzegorz Lisak,Victor W.C. Chang, Teik-Thye Limb,. Fate and distribution of heavy metals during thermal processing of sewage sludge. Fuel 226 (2018) 721–744.

[283] Nakic D. Environmental evaluation of concrete with sewage sludge ash based on LCA. Sustainable Production and Consumption 16 (2018) 193–201.

[284] Ciarán J. Lynn RKD, Gurmel S. Ghataora. Environmental impacts of sewage sludge ash in construction: Leaching assessment. Resources, Conservation & Recycling 136 (2018) 306–314.

[285] Wenlin Yvonne Lin WCN, Belinda Shu Ee Wong, Serena Lay-Ming Teo, Gayathiri d/o Sivananthan, Gyeong Hun Baeg, Yong Sik Ok, Chi-Hwa Wang. Evaluation of sewage sludge incineration ash as a potential land reclamation material. Journal of Hazardous Materials 357 (2018) 63–72.

[286] Oliver Krüger CA. Recovery potential of German sewage sludge ash. Waste Management 45 (2015) 400–406.

[287] Barbora Krejcirikova LMO, Gunvor M. Kirkelund, Carsten Rode,Ruut Peuhkuri. Characterization of sewage sludge ash and its effect on moisture physics of mortar. Journal of Building Engineering 21 (2019) 396–403.

[288] Jiang-shan Li ZC, Qi-ming Wang, Le Fang, Qiang Xue, C.R. Cheeseman, Shane Donatello,Lei Liu, Chi Sun Poon. Change in re-use value of incinerated sewage sludge ash due to chemical extraction of phosphorus. Waste Management 74 (2018) 404–412.

List of Tables

List of Figures