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Review

Recent advances and viability in sustainable thermochemical conversion of sludge to bio-fuel production

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ABSTRACT

Thermochemical methods are regarded as promising approach for managing sludge, that can achieve resources and energy recovery, volume reduction followed by efficient elimination of microorganisms. This review highlights an extensive description of the implementation of thermochemical technologies involving pyrolysis, gasification and hydrothermal liquefaction for valorisation of sludge into bio-fuel thus reducing the issues related to surplus generation and accumulation of sludge in environment affecting human health followed by rapid depletion of energy resources. The paper addresses working mechanism of thermochemical processes, their implementation for sludge conversion to bio-fuel and common factors affecting the process efficiency. Various studies have proved possible potential of thermochemical techniques for conversion of sludge to bio-fuel obtaining a high yield of bio-fuel and syngas. However, few technical challenges are still there that requires further studies and understanding for a better commercialization on industrial-scale and subsequently the future perspectives have also been analysed. Data collected from existing studies revealed that hydrothermal liquefaction has the efficiency to be proved better than other thermochemical technologies for proper valorisation of sludge resulting in high bio-fuel yield.

1. Introduction

The rapid rate of urbanization and growing population has imposed significant challenges to sustainable development. On one side, the increasing volume of municipal wastewater has generated significant amount of residual sludge that demands adequate technologies for treatment whereas on another side, rising energy consumption and associated problems have directed the requirement for energy and fuel diversification along with renewable and clean technology application [1,2]. According to recent statistics of Central Pollution Control Board (2021), the total amount of sewage sludge generation is around 72,368 million of liters per day in India. Moreover, the variation in prices of fossil fuels and excessive depletion similar to energy productivity followed by enhanced carbon footprint has led to a rise in emission of greenhouse gases and so on global warming. Therefore, inventing new substitute of renewable fuel resources and advanced methods for energy production that can effectively be carbon neutral has acquired the increased interest of researchers from the last few years [3].

Particularly, sludge can be defined as an unavoidable by-product released from wastewater treatment plants and is further considered as biomass feedstock for recovery of resources and energy like biodiesel, fuel gas, biogas, bio-oil, syngas, nutrients, biofertilizers, hydrolytic enzymes, heavy metals, biochar, ash etc. due to its great organic and beneficial inorganic content. Generally, it includes 59–88% (w/v) of organic matter, comprising 50–55% of carbon, 25–30% of oxygen, 10–15% of nitrogen, 6–10% of hydrogen with small traces of phosphorous and sulphur. Simultaneously, few minerals like calcium, iron, magnesium, potassium and heavy metals are also found in sludge.

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However, sludge also constitutes huge proportion of pathogenic microorganisms and toxic organic matters thus its mishandling may lead to serious concerns of atmosphere, water and land pollution with great influence on environmental feasibility [4]. Hence, the surplus generation of sludge from wastewater treatment plants and its accumulation in environment demands sustainable technologies for treatment.

To deal with these, various conventional methods like landfilling, incineration, anaerobic digestion etc has been practised and studied widely for decades. However, such methods are further associated with several flaws for instance, landfilling is most popularly known method for disposal of sludge but leaching is the major issue that arise through landfills and is somehow unavoidable thus possessing a threat to groundwater contamination. Additionally, emissions of fugitive methane to the atmosphere from landfills is also a matter of concern as methane holds high potency for causing global warming and the opportunity of recovering valuable nutrients from sludge is further lost after landfilling. Moreover, landfills are also becoming costly due to reduction in availability and high prices of land worldwide. Similarly, incineration is another commonly known method resulting in around 70% of the volume reduction followed by inactivation of toxic organic components and pathogens due to high operating temperature. But the leftover ash after incineration may constitute toxic compounds and require subsequent disposal in landfill. In addition, strict regulations with respect to concentration of air pollutants emitted into the environment further makes this technology a high-priced choice [5]. Furthermore, anaerobic digestion is another biological method that involves various steps to disintegrate organic feed for the production of biogas [6]. However, this biological process is relatively slow because the sludge requires retention for around 10 to 20 days. Additionally, the method and its products are sensitive and dependent on operating parameters and characteristics of feed as the microbes require optimum pH and temperature for effective functioning [7,8].

Consequently, thermochemical conversion technologies like gasification, pyrolysis and hydrothermal liquefaction have been regarded as attractive alternatives for recovering energy and renewable resources from sludge. These techniques not only provide immense reduction in volume, but also significant inactivation of pathogenic micro-organisms [9]. Moreover, the primary aim of thermochemical methods is the valorization of sludge into energy-rich content thus minimizing the negative impacts on environment [3]. Although, the process or equipment of these methods are complex but they reveal great efficacy and economic performance as compared to other methods [10]. Specifically, pyrolysis is beneficial for decreasing waste volume, neutralizing pathogens and degrading organic pollutants. The pyrolysis of sludge basically yields light gases involving hydrogen, carbon dioxide, carbon monoxide, methane, char and bio-oil [11]. Similarly, gasification is another thermochemical technique responsible for generation of syngas and is also an efficient way for hydrogen production [12]. Likewise, hydrothermal liquefaction has also been recognized as a promising method for generating novel biofuels directly from wastes and biomass. This particular method is capable of converting wet or dry biomass, as water is reaction medium thus reducing the additional cost related to drying and increasing feedstock flexibility [13]. Nonetheless, various existing studies have reviewed and investigated the promising potential of these thermochemical methods for recovery of energy and resources from sludge. However, some technical challenges related to this are still not confronted and demands more work for a better understanding and industrial-scale commercialization.

This review article deals with the current understanding of sludge valorization by different thermochemical processes i.e., pyrolysis, hydrothermal liquefaction and gasification for recovery of renewable resources and energy along with common factors that significantly influence the efficiency of these technologies. Moreover, it also highlights some of the technical challenges that are yet not approached and requires more attention for a wide scope in upcoming years.

2. Sludge and its characteristics

Sludge can be defined as an unavoidable by-product released from wastewater treatment plants comprising various solid particles dispersed in an impure water medium [8,14]. Generally, sludge has unique physico-chemical properties, including high moisture content, high ash content, low heating value, density, and viscosity [3]. It possesses extremely high proportion of water to solids, is comparatively pumpable, homogeneous and reveals rheological characteristics of "Bingham plastic". Wastewater from domestic, industrial or municipal sectors are regarded as main sources of sludge [15]. As per an estimate, sewage sludge is generated at a rate of 0.1–30.8 kg per population equivalent per year [8]. Moreover, the solid substances present in sludge are complex mixtures of inorganic and organic matter like metals, carbohydrates, proteins, fats and oil followed by huge range of dead and living microorganisms [16].

Nonetheless, sludge because of its great organic and beneficial inorganic content is considered as biomass feedstock for recovery of resources and energy like hydrolytic enzymes, heavy metals, nutrients, ash, biofertilizers, biodiesel, biogas, fuel gas, syngas, bio-oil etc [14] as shown in Fig. 1. Various existing studies have revealed possible potential of sludge released from wastewater treatment plants as a sustainable and renewable biomass source for production of energy [17]. However, the characteristics of sludge are highly influenced by numerous factors like wastewater properties, environmental legislation, type of pollutant entering the treatment plant, type of treatment system applied in wastewater treatment plant (WWTP), processing stage, water reclamation requirements and seasonal variations [8]. Moreover, on the basis of treatment stage, sludge is categorized into four different types namely, primary sludge, secondary sludge, mixed sludge and digested sludge. Table 1 depicts characteristics of different sludge.

Despite of all these advantages, mishandling of sludge possess a harmful effect to the ecosystem thus affecting environment sustainability. For instance, the organic and inorganic nitrogen present in sludge can lead to acid rain and disruption of ozone layer due to formation of NO_2. Similarly, phosphorus and nitrogen transferred by rainwater can found its way in waterbodies thus causing eutrophication. Additionally, the entrance of heavy metals in human body through food chain can lead to consequential health issues as shown in Fig. 2.

Hence, there is an immediate requirement to execute efficient ways for safe disposal and treatment of sludge [4]. On that account, various sludge utilization or disposal methods like incineration, landfill etc. came into existence. However, all such techniques further possess environmental risk related to public health.

For example, incineration can lessen the load of sludge by 70% but the release of exhaust gases into environment can leads to several environmental problems like emission of heavy metals, global climate change and formation of acid rain [18,19]. It is further considered as an expensive method of sewage disposal as it requires drying or dewatering of feed [20]. Similarly, the application of pyrolysis is also held back because of increased gate costs [3]. Therefore, from the viewpoint of environment sustainability and economic feasibility, recovering resources and energy from sludge by thermochemical conversion is highly promising. The primary aim of thermochemical methods is valorization of sludge energy content thus reducing environmental impacts for increased stiff standards. Nonetheless, the evolution of thermochemical methods are global players that set outs a global market.

3. Thermochemical conversion of sludge to bio-fuel

From the last few years, thermochemical techniques are regarded as an efficient way for producing valuable products and energy from residues of waste. Sludge generated from wastewater treatment plants, in its dry form can be reviewed as a distinctive example of biomass because of increased organic content and high calorific value [3]. Moreover, such techniques are also advantageous in managing sewage sludge, efficient

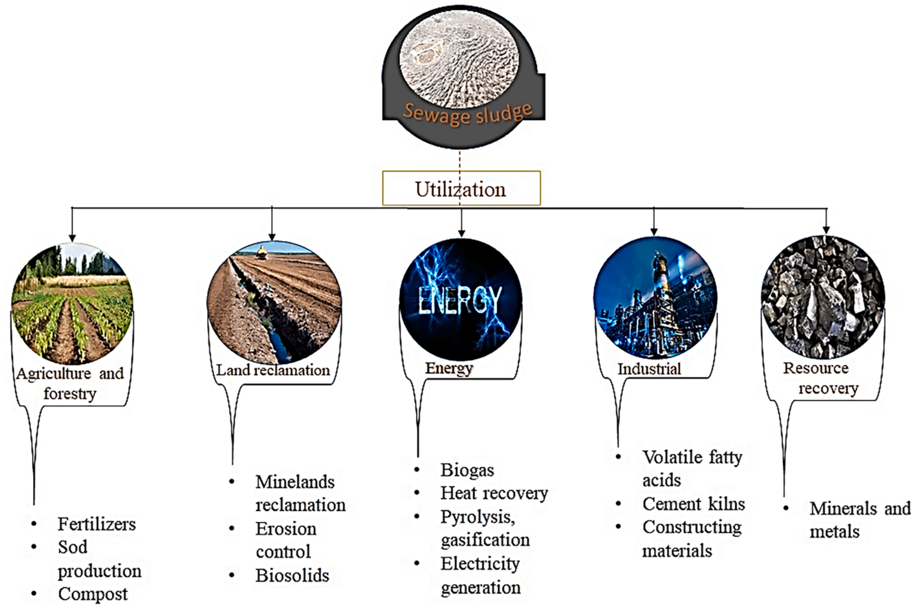

Fig. 1. Utilization of sludge in various sectors.

Table 1
Characteristics of different types of sludge.

S. No.	Sludge Type	Description	Chemical Constituent								Reference
			Ash (% db)	C (% db)	H (% db)	N (% db)	O (% db)	S (% db)	HHV (MJ/Kg)	Protein (% db)	
	Primary Sludge	Sludge which is obtained after primary treatment of sewage	42.02	45.2	7.3	9.3	32.1	–	20.04	–	[21]
	Secondary Sludge	Biologically activated sludge	76.60	47.18	7.18	6.70	35.75	3.19	19.87	41.90	[22]
	Digested Sludge	Treated sludge obtained after aerobic and anaerobic digestion	60.3	20.9	2.5	1.9	13.5	0.8	5–10		[23]
	Mixed Sludge	Mixture of primary and secondary sludge	–	43.39	6.48	5.04	–	0.8	20	30	[3,24]

db - dry basis, C- Carbon; H- Hydrogen; N- Nitrogen; O- Oxygen, S- Sulphur, HHV- Higher heating value.

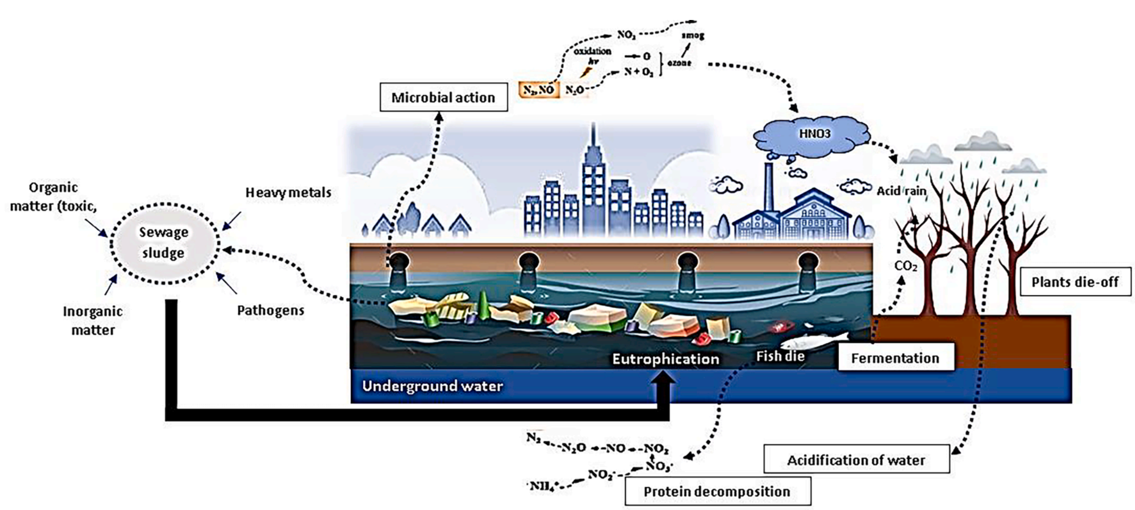

Fig. 2. Environmental impact of sewage sludge [4].

reduction of pathogens, notable volume reduction etc [8,9].

These types of thermochemical technologies mainly involve pyrolysis, hydrothermal liquefaction, incineration and gasification [25]. Generally, the selection of thermochemical technologies is influenced by various factors like economic aspects, desired form of target products, quality and type of feedstock, local emission standards etc [4]. Some of the thermochemical technologies along with their working principles are briefly outlined further.

a. Hydrothermal liquefaction

Hydrothermal liquefaction is a type of thermochemical technique which involves exposure of biomass to high pressure of around 5–20 MPa under an average temperature of 200–374 °C. During this process, the organic feedstock breaks into four components, namely target product i.e., bio-oil or biocrude oil, gas residue, aqueous phase and solid residue due to various polymerization reactions like hydrolysis, deoxygenation, repolymerization, fragmentation, aromatization and dehydration [26]. Basically, the conceptualization of hydrothermal liquefaction is to grasp the benefit of chemical and physical interactions between targeted reactants and water molecules such as its improved solvation ability and molecular properties like ionic product and dielectric strength change to increase the extraction of particular organic components such as carbohydrates, gases, proteins and fatty acids [27]. Additionally, on the basis of operating temperature it is classified into hydrothermal gasification, hydrothermal liquefaction and hydrothermal carbonation. However, in among all these, hydrothermal liquefaction has been considered as the most efficient approach for converting biomass into fuel. Although, the yield of final product is dependent on operating parameters of HTL process and type of biomass used. This particular process offers numerous advantages like it is energy-efficient and around more than 70% of feedstock carbon can be recovered in the form of bio-char or bio-oil [28]. Moreover, this technology has the potential to convert high moisture biomass into biocrude in aqueous medium and hence do not need any preliminary drying processes followed by elimination of more than 50% oxygen resulting biocrude oil with a greater heating value varying from 30 MJ/kg to 40 MJ/ kg [29]. Particularly, during hydrothermal liquefaction of sewage sludge the three main steps listed below takes place as shown in Fig. 3:

- Firstly, depolymerisation of several biomolecules like carbohydrates, proteins and lipids into oligomer or monomer units takes place due to various dissolution reactions thus dissolving the macromolecules into smaller units in organic solvent or water through solvolytic or hydrolytic reactions accelerated by elevated pressure and temperature.
- Secondly, there is decomposition of oligomers or monomers through deamination, dehydration, cleavage, decarboxylation resulting in fragments formation of small molecules which are active and unstable. During this process, there is removal of amino acid content, loss of water and carbon dioxide. Moreover, it should be noted that decarboxylation and dehydration reactions lower the oxygen content in bio-oil by producing CO_2 and H_2O thus enhancing the energy density and stability of bio-oil product.
- Thirdly, rearrangement of lighter fragments takes place through polymerization, cyclization, and condensation resulting to new components i.e., bio-oil, solid residue and aqueous phase. If any stabilization agent like hydrogen is present freely in the process, then the free radicals will be capped producing bio-oil products with good stability and low molecular weights [4].

Fig. 4 depicts schematic representation of hydrothermal liquefaction involved in thermochemical conversion of sludge to bio-fuel. Recently, hydrothermal liquefaction has attracted the interest of researchers for producing biocrude oil or bio-oil and various existing studies have revealed possible potential of HTL process in thermochemical conversion of sludge to biofuel. For instance, Lin et al. [22] in their study observed that bio-oil extracted from secondary sewage or activated sludge reveals low oxygen content, higher nitrogen-containing components and low boiling point compounds in contrast with distilled sewage

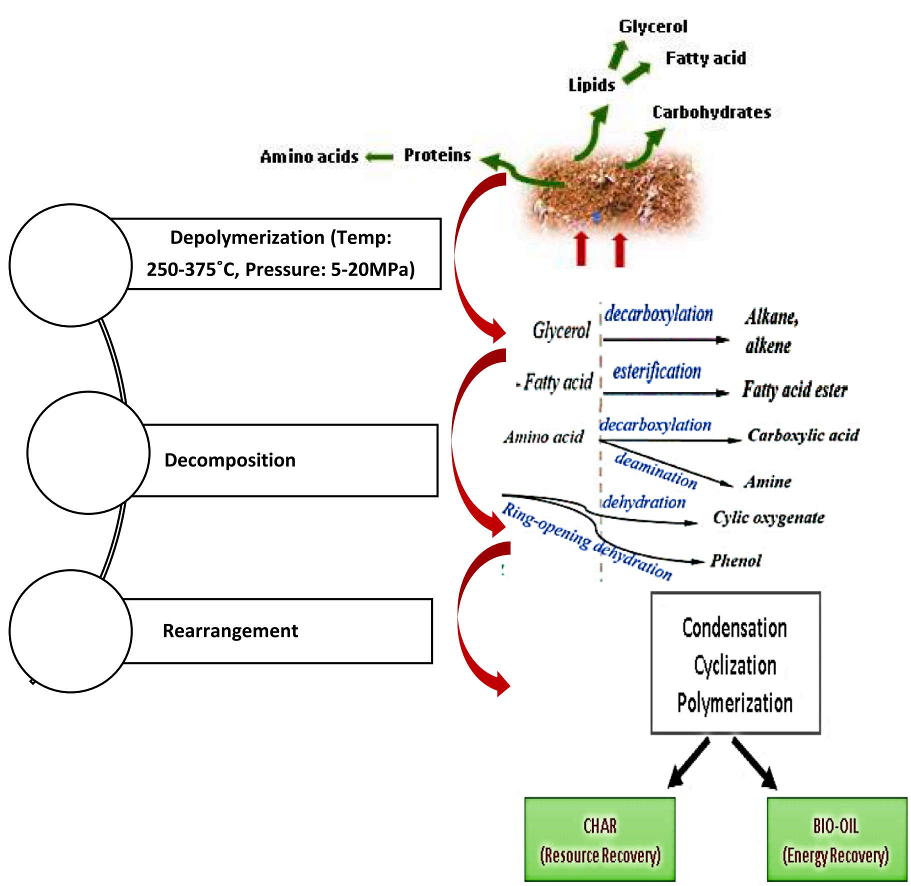

Fig. 3. Reaction pathway of hydrothermal liquefication of sludge conversion [3,4]

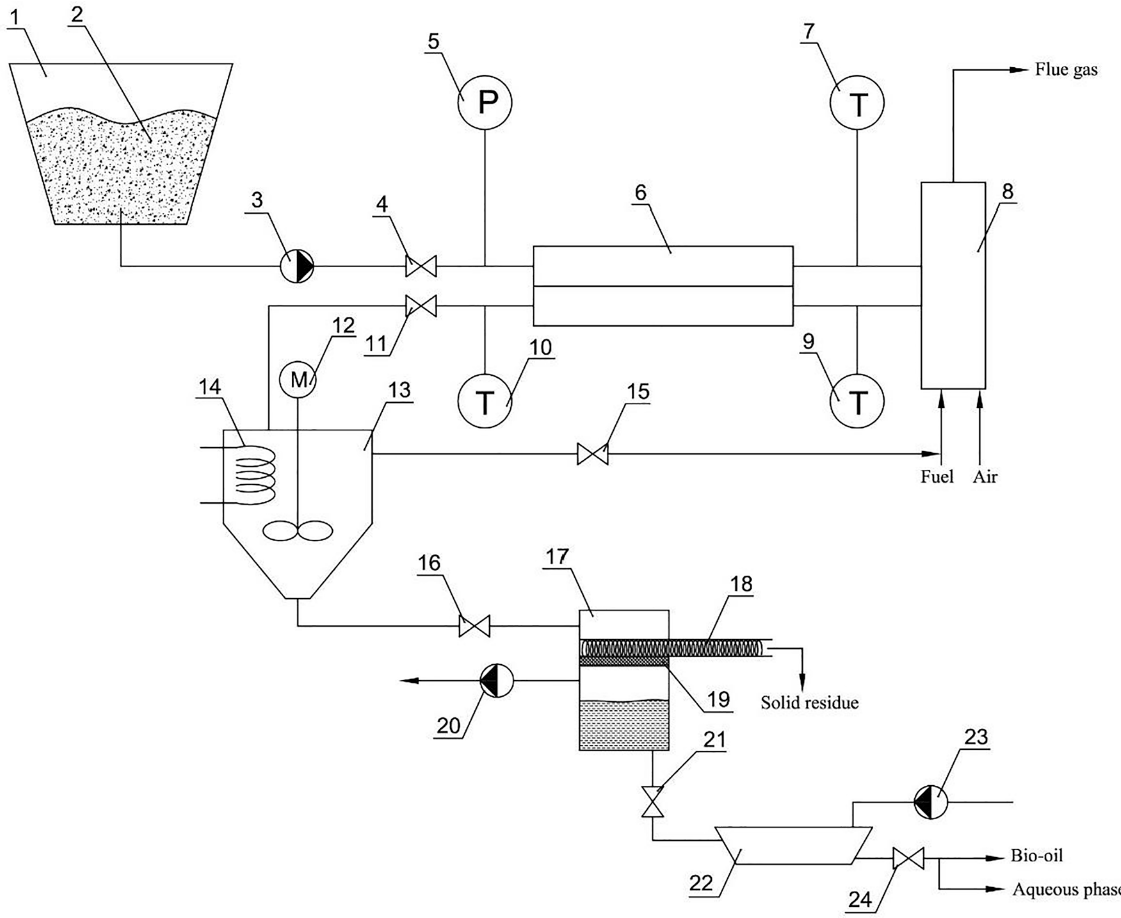

Fig. 4. Schematic representation of hydrothermal liquefaction for thermochemical conversion of sludge to bio-fuel. 1 – bunker, 2 – biomass raw, 3 – high-pressure pump, 4, 11, 15, 16, 21, 24 – valves, 5 – pressure sensor, 6 – heat-exchanger, 7, 9, 10 – temperature sensors, 8 – heater to set temperature, 12 – mixer, 13 – receiver for HTL products, 14 – cooler, 17 – nutsche filter, 18 – screw, 19 – filter, 20 – vacuum compressor, 22 – decanter, 23 – compressor.

sludge bio-oil. Additionally, the calorific value was higher (38.13 MJ kg^{-1}) much close to that of petroleum fuel. Hence, it was concluded that implementation of HTL can be a useful insight in bio-oil industry. Similarly, Seiple et al. [30] stated that HTL process is suitable at wastewater treatment plants by utilizing around 79% of complete recoverable dry solids of wastewater as a reliable feedstock to commercially produce 3.67 GL/y of biocrude intermediate. Therefore, this particular process can increase the energy, financial and environment feasibility of sludge treatment while minimizing the environmental risk and cost of operation and disposal. Kumar et al. [21] also

Table 2
Hydrothermal liquefaction for conversion of different sludge to bio-fuel and its elemental analysis.

S. No.	Sludge type	HTL process parameters	Bio-fuel yield	Elemental analysis of extracted bio-fuel				Reference
				C (wt %)	H (wt %)	N (wt %)	HHV/CV (MJ/kg)	
	Dewatered sludge	340 ℃ for 40 mins along with CTAB–AEO_9–SCW pre-treatment	47.6%	75.5	10.4	2.9	37.2	[31]
	Fish sludge	350 °C (sub-critical conditions)	59.11 $(-)_{daf}$	71.65	10.51	6.97	36.17	[13]
	Sewage sludge	350 °C for 15 mins	12.0%	_	_	_	32.1	[32]
	Secondary sewage sludge	350 °C (sub-critical conditions)	44.46 $(-)_{daf}$	73.02	10.53	5.18	36.65	[13]
	Paper mill sludge	340 ℃	44%	32.04	4.10	1.12	5.93	[33]
	Municipal sludge	325 ℃ for 30 min using FA as a green liquid hydrogen donor	41% to 62%	_	_	_	39	[24]
	Municipal sludge	Under ethylene ambience at 350 ℃ without any catalyst	41.6 wt%	59.37	7.62	4.80	29.57	[34]
	Sewage sludge	260 ℃, 40 min for first stage and 340 ℃, 40 min for second stage	42.2%	74.26	9.35	4.24	36.62	[35]
	Digested anaerobic sludge	300 ℃, 10–12 MPa and 30 min reaction time	9.4%	66.6	9.2	4.3	32.0	[36]
	Domestic sewage sludge	325 °C, 75:25 wt% (KMC4: DSS) and 45 min	39.26%	76.77	10.6	3.38	39.47	[37]

CTAB–AEO_9–SCW- Cetyl trimethyl ammonium bromide-alcohol polyoxyethylene ether-subcritical water; C- Carbon; H- Hydrogen; N- Nitrogen; HHV- Higher heating value; CV- Calorific value; $(-)_{daf}$- Dry ash-free basis; WWTP- Wastewater treatment plant; FA- Formic acid; DSS- Domestic sewage sludge; KMC4- Microalgal biomass (*Monoraphidium* sp. KMC4).

performed the hydrothermal liquefaction of municipal sewage sludge for recycling of organic nutrients and energy recovery from aqueous phase and concluded that HTL of municipal sewage sludge for 45 min at 255℃ in combination with titanium dioxide produced bio-crude with yield of 20.7%. Furthermore, the rate of energy recovery and high heating value was 34.27% and 28.12%, respectively. Utilization of hydrothermal liquefaction for conversion of different sludge to bio-fuel and its elemental analysis is mentioned in Table 2.

b. Pyrolysis

The term *"pyrolysis"* comprises of two Greek words i.e., *"pyro"* meaning *"fire"* and *"lysis"* meaning *"disintegration into integral parts"* [38]. Briefly, pyrolysis can be defined as the method of thermal degradation of chemical molecules taking place in an inert atmosphere and high temperature including the breakdown of high molecular chemical substances into simpler molecules generating oil, gaseous and solid fractions [39]. In this process, the temperature range, varies from 300℃ to 900℃ and sewage sludge after pyrolysis gets converted into ash, fixed carbon, bio-oils, water vapours and combustible gases. Moreover, the products obtained from pyrolysis can be divided into three categories:

- Solids which mainly contains ash and solid carbon along with significant quantity of heavy metals;
- Liquids (oil and tar), specifically, organic acids, aromatic compounds, water, acetic acid, hydrocarbons, aliphatic alcohols and carbonyl compounds containing phenols of high molecular weight;
- Non-condensable or stable gases which mainly includes carbon dioxide, methane, carbon monoxide, hydrogen and low molecular weight hydrocarbons in small concentrations [3].

Particularly, this technology is gaining much attention as it can generate py-gas or pyrolysis gas as renewable fuels, crude bio-oil also called as bio-oil, and a relevant soil amendment product called as biochar [40]. Additionally, with respect to clean gas emissions, it is an environment friendly technique as compared to extensive implementation of incineration and combustion. Generally, pyrolysis of organic compounds like plastics, lignocellulosic and municipal wastes has sustained prolonged attention because of their capability to transform such wastes into valuable chemicals and useful energy. Recently, pyrolysis of sewage sludge has also received great attention as an environmentally and economically sustainable technology for advantageous utilization of sludge. Furthermore, pyrolysis of sewage sludge presents the advantage of concentrating heavy metals (excluding cadmium and mercury) present in final residue [3].

During treatment of sludge through pyrolysis, firstly heat is transferred to surface of particles present in sludge either by convection or radiation and then slowly to interior of particle. When these sludge particles undergo transient heating, there is a specific increase in temperature, initially leading to evaporation of moisture and then secondly to progressive release of pyrolytic volatiles known as primary pyrolysis stage. Mainly, the generation of primary volatiles is due to thermal dissolution of chemical bonds present in sewage sludge organics like lipids, carbohydrates and proteins. Pyrolytic volatiles mostly comprise of methane, hydrogen, water, carbon monoxide, carbon dioxide, condensable organic components and another non-condensable hydrocarbon as shown in Fig. 5 [19].

Protein present in sewage sludge possess various pathways as compared to those of plant residues. Dehydrogenation and deamination can cause protein decomposition along with disappearance of –CHON– in SSBBs and release of gaseous nitrogen compounds like ammonia [41]. The remaining carbon-rich solids turns into biochar constituting a notable amount of mineral matter initially present in sludge. With a further increase in temperature, few products of primary pyrolysis can take part in different secondary reactions forming secondary products as resource and energy recovery [4]. Inorganic mineral substances take part in sludge pyrolysis through three main pathways:

- Thermal decomposition of mineral compounds;
- Interaction between nitrogen-containing and mineral compounds;
- Sludge degradation by catalytic effect of mineral oxides [42]

Moreover, the difference between primary and secondary pyrolysis is not clear because secondary reactions can take place in particles pores as well as in bulk gas. Therefore, primary and secondary reactions can take place at same time in various parts of feedstock particles. Char obtained from primary pyrolysis can act as catalyst and adsorbent in secondary reactions thus converting organic vapours into secondary char and light

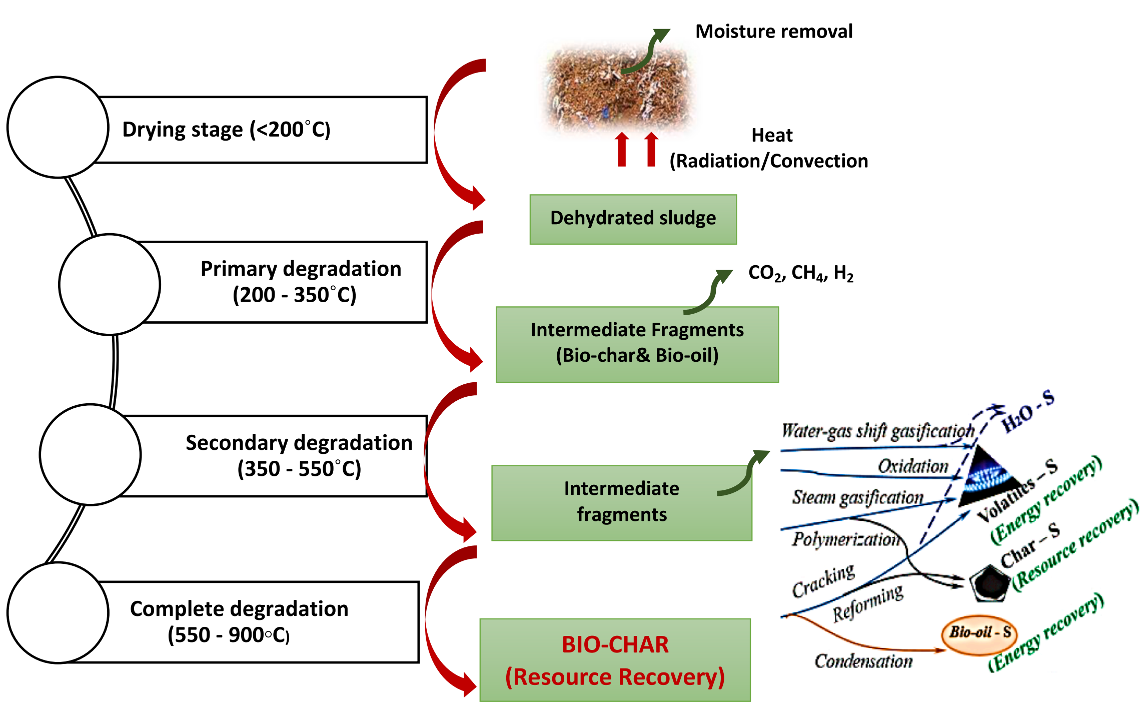

Fig. 5. Reaction pathway of pyrolysis of sludge conversion [3,4]

gases [4]. However, the working mechanism of pyrolysis is yet not fully acknowledged mainly in area of wet sludge [3].

Pyrolysis is further divided into various types, namely fast pyrolysis, slow pyrolysis, flash pyrolysis, catalytic pyrolysis and catalytic hydro-pyrolysis. Table 3 reflects the influence of different types of pyrolysis. Fig. 6 shows schematic representation of pyrolysis involved in thermochemical conversion of sludge to bio-fuel.

In fast pyrolysis, the residues of biomass are heated under high temperature in absence of oxygen. This process offers 60–75% of liquid biofuels along with 15–25% of biochar residues based on initial biomass weight. Furthermore, it can provide 10–20% of gaseous phase on the basis of biomass used and the process can be distinguished by small vapour retention time. Flash pyrolysis is also another type of pyrolysis process in which bio-oil production can reach up to 75%. This method is executed by speedy devolatilization in inert atmosphere by applying high heating rate under high temperature of around 450℃ and 1000 °C. However, this process possesses poor thermal stability and due to catalytic effect of char, oil turns viscous and also contains few solid residues sometimes. Additionally, slow pyrolysis is third type that can produce charcoal of good quality under low heating rates and low temperature. In this process, the time of vapour residence can be about 5–30 min and quality of bio-oil produce is very low. Slow pyrolysis faces low heat transfer values followed by long retention time resulting in increased expenditure by high energy input [38]. Catalytic fast pyrolysis could be applied to generate aromatics by using different types of lignocellulosic feedstocks. It reveals various advantages over other process as the pyrolysis can take place in single reactor excluding the involvement of expensive catalysts [43]. Moreover, catalytic hydro-pyrolysis is a type of catalytic pyrolysis in which the process is executed in fluidized bed reactor using hydrogen gas flow. It involves the replacement of fluidized bed by transition metal catalyst. As per the reports, bio-oil can be transformed into low molecular weight hydrocarbons under short contact time by substituting inert sand with nickel-based catalyst at atmospheric pressure [38].

Various studies have demonstrated the possible potential of pyrolysis process in thermochemical conversion of sludge to bio fuels like, Luo et al. [44] analysed the effect of various organics/ash and C/H/O ratios on properties microwave pyrolysis to produce bio-fuels and stated that a mixture of sludge containing different organic/ash ratios can be pyrolyzed to achieve high energy efficiency and high-quality bio-fuels. Similarly, Ghodke et al. [45] performed the pyrolysis of sewage sludge for producing sustainable and environment friendly fuels followed by value-added biochar products. The results revealed that product yield of 22.4 wt% bio-oil, 58.7 wt% biochar and 18.9 wt% pyrolysis gases at around 500 °C. In addition, bio-oil revealed a lower O/C ratio (1.10) and greater H/C ratio (3.49) which indicated its suitability for engine use. McIntosh et al. [46] also studied the effect of pyrolysis in combination with sulphided $NiMo/Al_2O_3$ for producing biofuels from milk processing sludge. The result stated that under low pyrolysis temperature of around 450 °C, yield of bio-oil was increased by 57.7% and the obtained bio-oils were improved in aliphatic hydrocarbons 11–14% of alkenes, 19–22% of alkanes and 57–63% of alkyl nitriles. Additionally, the O/C molar ratio was lower (0.08 to 0.1) followed by a high HHV (40.8–41.8 MJ/kg) thus revealing possible fuel applications. Furthermore, Chen et al. [47] used low temperature pyrolysis for converting sewage sludge into clean solid fuel and evaluated that the fuel ratio of biochar was notably enhanced to 0.54 and O/C & H/C atomic ratios decreased to 0.33 and 0.76 by extending pyrolysis process. In addition, about 70% of sulfur and nitrogen was also removed. Utilization of pyrolysis for conversion of different sludge to bio-fuel and its elemental analysis is mentioned in Table 4.

c. Gasification

Gasification is also one of the thermochemical methods which involves conversion of carbonaceous content of fuel into ash and combustible gas under a net reducing atmosphere. The ideal target of gasification is to produce clean combustible gas under high efficiency [61]. Particularly, this process can be considered as an extension of pyrolysis, which primarily involves heating of feedstock withstanding pyrolysis and drying, emitting volatiles and leaving char as solid residues, accompanied by gas–gas and gas–solid reactions in presence of gasifying agent [4]. When there is gasification of sewage sludge, it undergoes various chemical and physical changes. During this particular process, single particle of sludge undergoes four main stages, namely drying, pyrolysis, oxidation and reduction which are briefly described further as shown in Fig. 7 [3].

- Firstly, drying takes place at around 70–200 °C to eliminate moisture. There are various factors which influence the drying rate like recirculation velocity, surface area of feedstock particle, temperature difference between hot gases and particle, internal diffusivity of moisture within sludge particle and relative humidity of drying gas.
- During pyrolysis or secondary step which occurs at around 350–500 °C there is thermal decomposition of organics when approximately 60 to 70 wt% of feedstocks can be transformed into char, gases and complex liquid fraction. Additionally, the product distribution is greatly influenced by heating rate, reactor temperature, gasification agent and chemical compositions of sewage sludge. Although, the proximate analysis of sewage sludge can be used to approximately estimate the quantity of char and overall yield of pyrolyzed products.
- Thirdly, there is occurrence of gas–solid reactions which converts char that is solid carbon into different gases like methane, carbon monoxide, carbon dioxide and hydrogen. The partial or carbon oxidation reactions are greatly exothermic, offering sufficient energy for pyrolysis and drying of including other solid–gas endothermic reactions. Additionally, hydrogenation reactions can also take place contributing to energy necessities of gasifier.
- In last step of gasification, homogenous gas–gas reactions occur which affects the configuration of final gaseous produce [62].

Fig. 8 depicts schematic representation of gasification involved in thermochemical conversion of sludge to bio-fuel. In addition, this method is helpful in decreasing the volume of sludge and hence enabling its disposal in a suitable form. It can be seen as an attractive substitute in contrast with prevalent related technology of incineration. Moreover, gasification can overcome the various flaws associated with incineration involving demand for supplemental fuel, emissions of nitrogen oxides, sulphur oxides, fly ash, heavy metals and the possible generation of chlorinated dibenzofurans and dibenzodioxins as it is a net chemically reductive process. Gasification of sludge produces combustible gas with high-quality which can further be burned for generation of power and producing heat for sludge drying.

Gasification has also been studied for thermochemical conversion of sludge to biofuels. Hu et al. [63] in their study used carbon dioxide as reaction gas during sub and supercritical water gasification of municipal sludge for converting sludge into biofuels. The results stated that lower heating value of bio-oil got increased by 6.32 MJ/Nm^3 and observed that combination with carbon dioxide possess the efficiency for optimizing sludge-derived biofuels quality and converting into carbonaceous fuels. Furthermore, Werle [64] performed the gasification of dried sewage sludge and indicated that the gas produced was of high lower heating value hence as a result the production of carbon monoxide and hydrogen was promoted. Utilization of gasification for conversion of different sludge to bio-fuel and its yield is mentioned in Table 5.

4. Common factors affecting the efficiency of thermochemical processes

Several existing studies have revealed various factors that significantly affects the efficiency of hydrothermal liquefaction, pyrolysis and gasification during thermochemical conversion of sludge into biofuels. Such type of factors include temperature, pressure, addition of catalysts,

Table 3
Influence of different pyrolysis methods.

S. No.	Pyrolysis type	Reaction conditions				Products obtained		Yield (wt.%)		Advantages	Limitations	Reference
		Heating rate (°C/s)	Vapour residence time	Feedstock size (mm)	Temperature (°C)	Main product	By-product	Main product	By-product			
1.	Slow pyrolysis	0.1–1	10–100 mins	5–50	300–700	Biochar	Bio-oil & gaseous products	~35	~30 (Bio-oil) 35 (gases)	• Finer char produced • Removal of pollutants like SOx, NOx etc. • Enhance C/N ratio & heating value of sludge • Suitable for solid fuel production & carbon sequestration	• Produced low quality liquid bio-oil • Cracking due to long residence time thus reducing bio-oil yield • Increased expenditure due to high energy input	[10,38,48-51]
a.	Faecal sludge slow pyrolysis		10, 20 & 40 mins		350, 450 & 600	Biochar		70.4, 62.6 & 58.3 at 350, 450 & 600 °C, respectively				
b.	Biological sludge slow pyrolysis	2 to 30	Regarding 10 mins as sufficient time		300 to 600	Biochar		0.40 to 0.73 kg kg^{-1} dry sludge				
2.	Fast pyrolysis	10–200	0.5–5 s	Less than 3	400–800	Bio-oil	Char & gaseous products	~50	~20 (biochar) ~30 (gases)	• Sustainable scaling-up • Secondary transformation of additives or motor fuels • Produced biofuel utilized for industrial purposes like boiler, engine, turbine. • Simple transportability and storability of liquid fuels	• Low yield of gaseous products • Less heating value of produced gases	[10,38,50,52]
a.	Dry sewage sludge fast pyrolysis				487.5	Bio-oil		35.8				
3.	Flash pyrolysis	More than 1000	Less than 0.5 s	Less than 0.2	800–1000	Bio-oil	Char & gaseous products	~75	~12 (biochar) ~13 (gases)	• Maximize bio-oil production • Produced liquid fraction can be used as fuel or source for chemicals • Produced solid fractions can be utilized as adsorbent for wastewater treatment purposes	• Poor thermal stability • High oil viscosity due to catalytic effect of char • Presence of solid residues in oil	[38,50,51,53]
a.	Dry -sewage flash pyrolysis				450–600			77 at 500 °C.				
4.	Catalytic pyrolysis	Catalyst type and its ratio to feed dominantly affects the process and product yield				• Product distribution varies with type of catalyst employed • Bio-char yield enhanced by acidic catalyst • Basic catalysts responsible for higher bio-oil yield				• Catalysts enhance pyrolysis efficacy • Thermally stable bio-oil produced • Obtained bio-oil constitutes less oxygenated & acidic components • Secondary cracking produced liquid & gas phase	• Nickel and zeolites catalysts undergoes rapid deactivation due to coke formation • Some are highly expensive like noble metal catalysts	[4,10,54]
a.	Oily sludge catalytic pyrolysis					• Pyrolysis gas yield 31.46 L/kg with recovery rate of 48.21% for pyrolysis oil • Ni involvement improved pyrolysis gas yield						

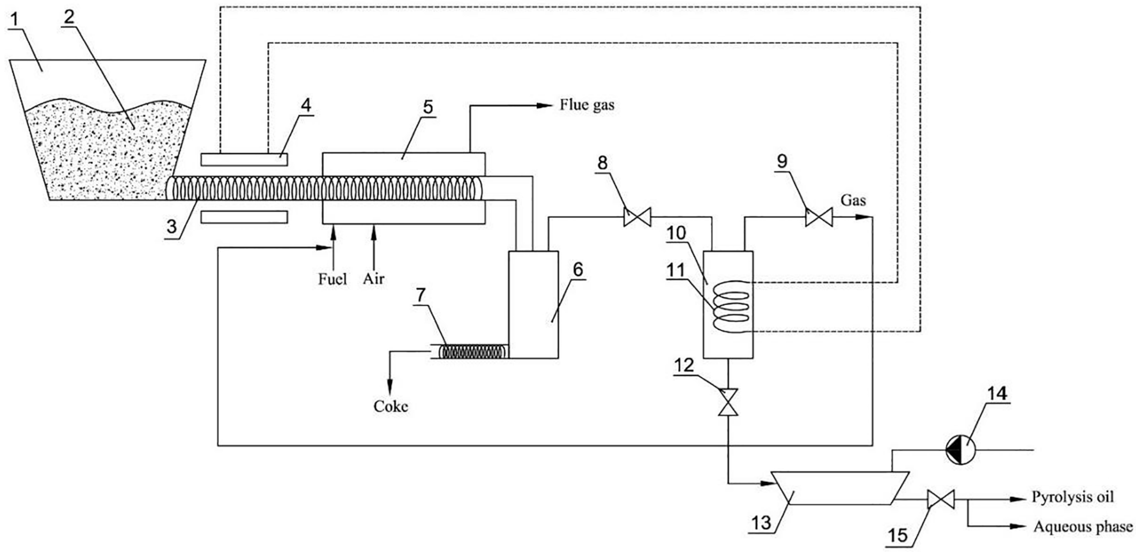

Fig. 6. Schematic representation of pyrolysis for thermochemical conversion of sludge to bio-fuel. 1 – bunker, 2 – biomass raw, 3 – feeding screw, 4 – heat-exchanger, 5 – pyrolysis reactor, 6 – receiver for pyrolysis products, 7 – screw, 8, 9, 12, 15 – valves, 10 – receiver for evaporated pyrolysis products, 11 – cooler, 13 – decanter, 14 – compressor.

Table 4
Pyrolysis for conversion of different sludge to bio-fuel and its elemental analysis.

S. No.	Sludge type	Pyrolysis process parameters	Bio-fuel yield	Elemental analysis of extracted bio-fuel				Reference
				C (wt %)	H (wt %)	N (wt %)	HHV/CV (MJ/kg)	
	Digested sewage sludge	15th at 487.5 ℃	35.8%	65.2	8.6	8.4	35.4	[52]
	Sewage sludge	450 to 600 ℃, with HZSM-5 catalyst to feed ratio of 2:1	20.9 wt%	_	_	_	_	[55]
	Mixture of LC & DSS	550 °C with heating rate of 10 °C min^{-1}	31 wt%	_	_	_	12.29	[56]
	Milk floatation sludge	450 ∘C for 45 mins	57.7%	76.50	11.8	3.57	41.79	[46]
	Sewage sludge	250, 350, 450, 500, 550, 600 & 700 ∘C with heating rate of rate of 10 ℃ min^{-1}	22.4 wt%	35.43	10.33	2.2	16.53	[45]
	Palm oil sludge	550 ℃ with a heating rate of 100 °C/min	27.4 wt%	_	_	_	22.2	[57]
	Sewage sludge	500 °C	77 wt% daf	45.0	8.8	6.6	_	[58]
	Sewage sludge + 40% rapeseed	450 °C for 15 mins with a heating rate of 25 °C/min	16.6%	63.8	11.7	4.6	34.8	[59]
	50 wt% sewage sludge and 50 wt% pinewood sawdust	500 °C	55 wt%	_	_	9.40	_	[53]
	Sewage sludge & rice husk	Co-pyrolysis at 550 °C	17.21 wt %	54.9	7.8	5.85	25.75	[60]

MWTP- Municipal water treatment plant; LTU- Leachate's treatment unit; STP- Sewage treatment plant; WWTP- Wastewater treatment plant; C- Carbon; H- Hydrogen; N- Nitrogen; HHV- Higher heating value; CV- Calorific value; UPES- University of Petroleum and Energy Studies; daf- Dry ash free basis.

residence time, particle size etc (Table 6).

a. Effect of Temperature

Out of the above stated factors, effect of temperature has been studied and acknowledged widely. Temperature is the principle controlling process parameter for gasification, pyrolysis and hydrothermal liquefaction of sludge. During gasification, it influences the Boudouard reaction, steam methane reforming reactions, completion of gasification reactions, methane formation, combustion and water gas shift reaction. Generally, the decomposition of methane includes reactions related to hydrocarbon reformation while due to steam reforming, methane decomposition and hydrocarbon reforming reactions the yield of hydrogen increase at a very rapid rate. In gasification, a large amount of char gets transformed into gaseous content under high temperature. Furthermore, at temperature of about more than 800 °C, the conversion rate of high molecular weight hydrocarbons and carbon will be higher for gas production and eventually cold gas efficiency would be enhanced [74]. However, excessively elevated temperature can result in clinker development due to high ash content of sludge [10]. Moreover, Lin et al. [75] regarded temperature as the most crucial parameter influencing the yield of produced bio-gas through gasification process. They observed that with an increase in temperature from 360 ℃ to 440 ℃, the yield of biogas also got increased from 44.6 L/kg sludge to 231.1 L/kg sludge, respectively. Hence, it was clearly indicated that with an increase in temperature, the efficiency of gasification process also got increased. Moreover, noticeable changes were also seen in yield of CO_2 and H_2 in biogas. At high temperature, supercritical water generated more •H and •OH radicals, out of which hydroxyl radicals oxidize the carbon element into a stable carbon dioxide gas and •H radicals favoured an increase in yield of H_2 gas.

Additionally, in pyrolysis there is maximization of liquid yield at a temperature of about 450–550 °C [58]. At a very low temperature, few chemical bonds are not powerfully sufficient to break down. Hence, some organic compounds do not degrade which can be understood by TGA analysis of sewage sludge. Furthermore, at above optimum temperature, secondary pyrolysis of volatiles is increased. Consequently, tar breakdown into light gases, giving an increased gas yield and a reduced liquid yield. At high temperature, this reduction in liquid yield is commonly companied by increased production of polyaromatic

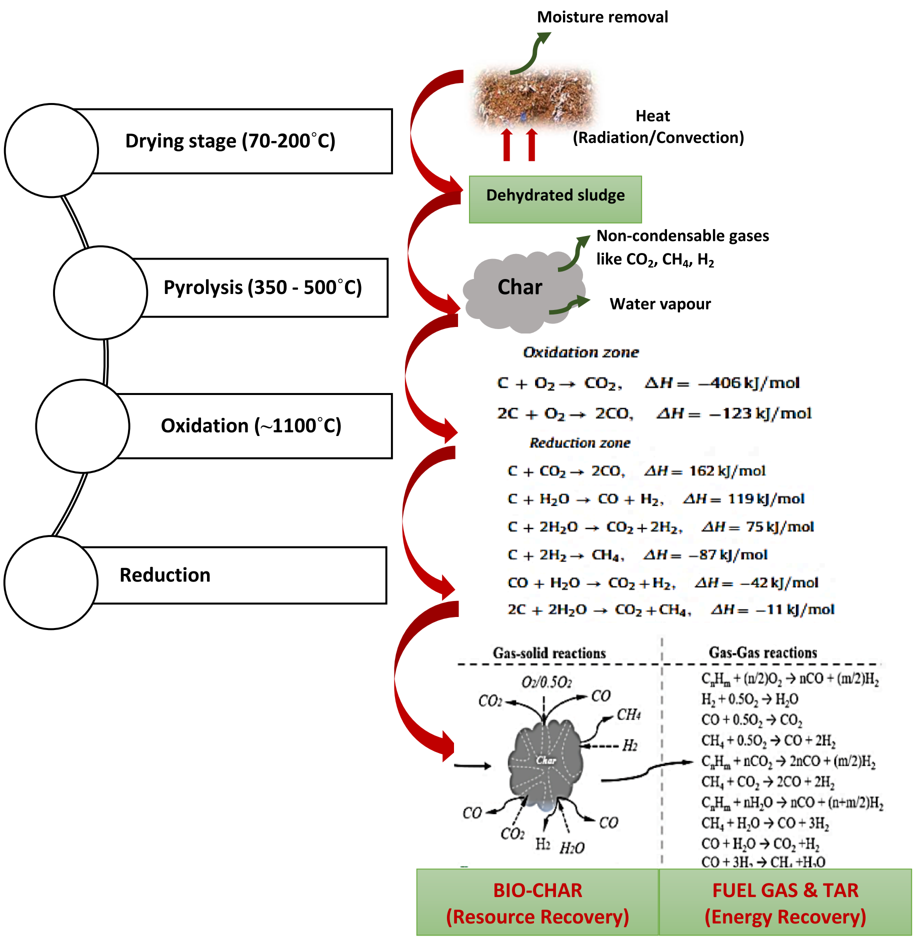

Fig. 7. Reaction pathway of gasification of sludge conversion [3,4]

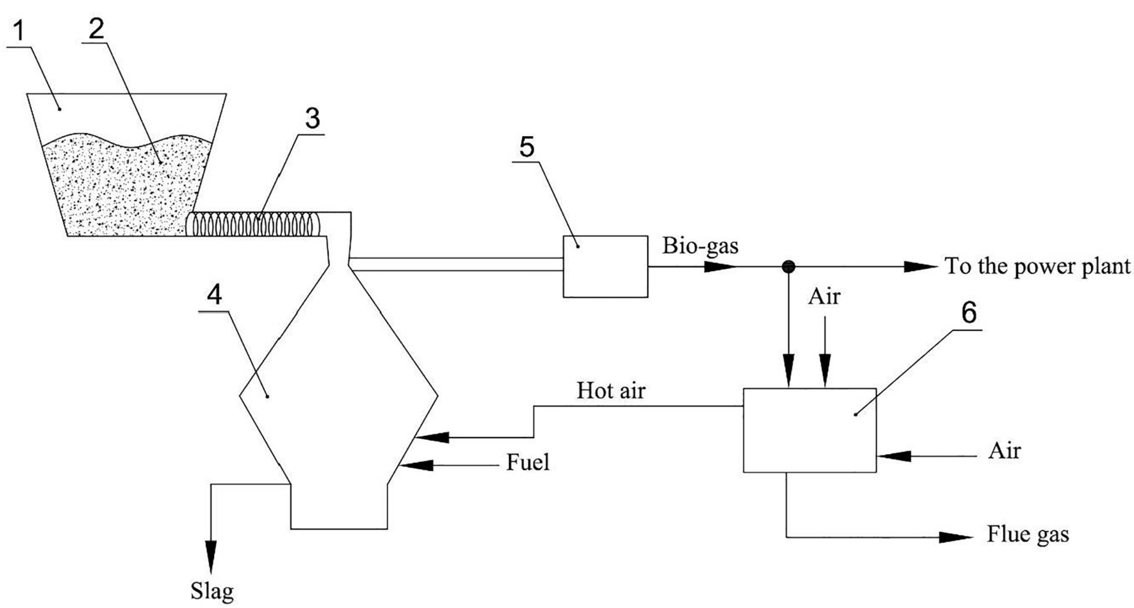

Fig. 8. Schematic representation of gasification for thermochemical conversion of sludge to bio-fuel. 1 – bunker, 2 – biomass raw, 3 – feeding screw, 4 – gasification reactor, 5 – filtering system, 6 – heat-exchanger.

hydrocarbons. PAHs are formed by reactions between light hydrocarbons and low molecular mass tar components under high temperature [76]. On the basis of process temperature, pyrolysis can be categorized into two types i.e., liquefaction and gasification. In pyrolysis liquefaction, which takes place at around 425–575 ℃, there is 30–40 wt% production of bio-oil while in pyrolysis gasification which occurs at

Table 5
Gasification for conversion of different sludge to bio-fuel and its yield.

S. No.	Sludge type	Gasification type	Gas produced	Gas yield	Reference
	• Industrial wastewater sludge (IS) • Sewage sludge (SS)	Steam co-gasification	• Hydrogen	• 9.10 vol% to 12.46 vol %	[17]
	Dewatered sewage sludge	SCWG	• Methane	• 11.3% to 41.8%	[65]
	Oily sludge	Pyrolysis coupled with gasification	• Methane	• 3.25%	[54]
	• Sewage sludge • Torrefied biomass	Drying & autothermal gasification	• Hydrogen • Carbon monoxide	• 44.3% • 100.1%	[66]
	Sewage sludge	Solar steam gasification	• Hydrogen	• 61.2–67.6 g/kg(sludge)	[67]
	Sewage sludge + CaO pellets	Two-stage sorption-enhanced steam gasification	• Hydrogen (1st stage) • Carbon monoxide (2nd stage)	• 72.2 vol% purity • 60.5 vol% purity	[68]
	• Sewage sludge (SS) • Palm oil empty fruit branch	SCWG	• Hydrogen • Methane • Carbon dioxide • Carbon monoxide	• 32.2% • 27.0% • 86.0% • 4.5%	[69]
	Municipal sludge		• Hydrogen • Methane • Carbon dioxide • Carbon monoxide • Nitrogen	• 23.3 (v/v. %) • 1.2 (v/v. %) • 13.4 (v/v. %) • 18.5 (v/v. %) • 43.6 (v/v. %)	[70]
	Activated sewage sludge + RNi-Mo2 catalyst	_	• Hydrogen	• 18.13 mol/kg dry • sludge	[71]
	Sewage sludge	Gasification system using waste heat of BF slag	• Hydrogen	• 35.3%	[72]

STP- Sewage treatment plant; WWTPs- Wastewater treatment plants; SCWG- Supercritical water gasification; MWWTP- Municipal wastewater treatment plant; RNi-Mo2- Raney-nickel-Mo2; BF- Blast furnace.

more than 650 ℃, there is 51 to 66 wt% production of bio-gas of dry sewage sludge [3]. For instance, Huang et al. [77] in their study concluded that during pyrolysis of granular sewage sludge a temperature of around 600 ℃ was suitable for complete decomposition of sludge thus producing increased quantities of bio-oil. In addition, temperature of above 600 ℃ favored the production of bio-char and yield of bio-oil increased from 38.8 % to 43.4 % with an increase in temperature from 500 °C to 600 °C which got decreased with further increase in temperature. Hence, a temperature of 600 °C was regarded as most appropriate for bio-oil production.

Similarly, in hydrothermal liquefaction, temperature is one of the most crucial factors that not only influence the bio-fuel yield but also exerts a great effect on bio-oil properties. With a rise in temperature, there is protein hydrolysation followed by deamination of amino acids thus producing ammonia and organic acids or decarboxylation generating carbon dioxide and amines. Initially, at around 150 ℃, there is increment in concentration of amines and with further increase in temperature, the yield of acetic acid got enhanced followed by production of furfural derivatives, alcohols, ketones, acids, N-O heterocyclic components and amides due to reaction of carbohydrates and fatty acids with amino acids. All these produced reactants comprise the main portion of bio-oil [73]. Like, Xu et al. [78] in their study observed that during hydrothermal liquefaction of sewage sludge, the yield of bio-crude oil increased significantly at temperature from 260 ℃ to 340 ℃ and attained a maximum value of 22.9 wt% at 340 ℃. However, at 350 ℃ a slight drop of around 3.0 wt% was recorded because of the more gas production by biocrude conversion.

b. Effect of gas residence time

The effect of gas residence time on sludge gasification has also been studied by researchers. An increment in the efficacy of sludge gasification with increase in bed height has been reported. The reason behind this fact is the reduction in reactivity of consuming char particles at delayed stage of their conversion. The leftover carbon is diluted in ashes and internal diffusion of gaseous components is inhibited by high ash content. Furthermore, due to increase in gas heating value with bed height there was steam reforming and volatiles cracking, as the volatiles were hold for longer in gasifier. To be particular, Amrullah and Matsumura [79] analysed the effect of residence time on efficiency of gasification process and concluded that with an increase in residence time, the yield of methane got increased by 10.5 to 28.8 vol% due to methanation which is favoured under long residence time while the yield of hydrogen gas got reduced by 35.1 to 13.9 vol% with time. The reason behind this fact is reaction between carbon monoxide and hydrogen gas for generating methane. Moreover, under high temperature from 550 to 600 ℃ and short residence time, hydrogen gas ranging from 38.5 to 39.4 vol% was produced as the target product as water–gas shift reaction is indulged at increased temperature and the yield of methane got increased with time under all temperatures thus indicating that a prolonged residence time favours the process of methanation.

The phenomenon of secondary pyrolysis can be minimized by a very short vapour residence time or by a quick quenching of volatiles. Studies have shown that short residence time under constant pyrolysis temperature increase the oil yield due to reduction in degree of secondary reactions. Although, it is important to keep thing in mind that short residence time can't simply be achieved by maximizing the flow of sweeping or fluidising gas. This is because constant increase in gas flow rate after a definite point will be responsible for dilution of tar concentration in vapour thus making condensation difficult which will be resulting in reduced yield of liquid [8]. In addition, Park et al. [80] stated that residence time of pyrolysis is one of the most critical parameters for bio-oil yield as it regulates the chances for secondary tar reactions. The study concluded that with an increase in feed rate or nitrogen flow rate the yield of bio-oil got enhanced due to decrease in vapor residence time. For instance, when the feed rate got doubled to 5 g/min, the yield of bio-oil got increased by 45.1 wt%.

Several studies have demonstrated the effect of residence times on hydrothermal liquefaction of sewage sludge. The period of reaction time may illustrate the substantial conversion of biomass and configuration of products. Generally, in supercritical water oxidation waste treatments, there is destruction of dilute organic components under supercritical pressure and temperature for short residence times. Nonetheless, optimization of residence time is a very important step for efficient degradation of organic components in biomass. Generally, for achieving high yield of liquid oil, it is important to retard the disintegration of lighter compounds. The products and radicals can be stabilized by addition of reducing agents like syngas, hydrogen and tetraline. The yield of oil can reach highest before reducing for extremely long residence times while biomass conversion and gas yield enhance constantly

Table 6
Comparison of different thermochemical techniques for sludge conversion.

S. No.	Technologies	Reaction conditions				Target product	By-product	Yield of main target product	Advantages	Limitations	Reference
		Operating temperature	Atmosphere	Pressure	Suitability for feedstock						
	Pyrolysis	300 to 650 ℃	Inert or oxygen free	Atmospheric	Dry sewage sludge	Bio-oil	Non-condensable gases, ash & solid carbon	51 to 80 wt % on daf	• Optimization of product distribution on the basis of operating conditions • Reduction in waste volume • Decomposition of organic pollutants • Neutralization of pathogens	• Low product quality due to high moisture content of sludge • Demands high energy consumption • Drying is time consuming • Accessibility of product for direct economic use	[5,10,51]
	Gasification	Above 650 ℃	Requires gasifying agent like CO_2, steam etc.	Atmospheric	Dry sewage sludge	Bio-gas	Char	51 to 66 wt % on db	• Promising route for H_2 production • Avoid the emission of hazardous compounds • Enhanced thermal efficiency • Produced bio-gas can be used for fuel as well as for chemical synthesis	• Low product quality due to high ash & moisture content • Energy consumption for drying is a main issue upon direct feeding of sludge into gasifier • Production of tar as by-product cause blockage of fuel injector nozzles, down-stream valves & pipelines	[10,51,63]
	Hydrothermal liquefaction	425 to 575 ℃	Presence of nitrogen gas	Elevated (5 to 20 MPa)	Wet sewage sludge	Bio-oil	Solid (biochar), aqueous phase fraction & gaseous materials	30 to 40 wt % on db	• Wet sludge can be utilized directly • Energy recovery rate is greater than 50% • Elimination of bioactive components • Inactivates antibiotic resistant genes • Low operating temperature as compared to other technologies	• Requires special reactor due to high operating pressure • Requirement of resistant materials for reactors fabrication • Reduction in bio-oil yield during evaporation of solvent • Increased capital cost	[4,51,73]

MPa- mega pascal; db- dry basis; daf- dry ash-free basis.

till saturation point [81]. To be specific, Tong et al. [35] stated that under low temperature conditions, elongation in residence time can enhance the yield of bio-oil. As per the studies, when residence time was 10 min for low temperature segment, the bio-oil yield got enhanced with increase in temperature followed by a reduction in yield of solid residue. On the other hand, when residence time got extended by 40 min under low temperature segment, the bio-oil yield commuted unevenly with rise in temperature. This might be due to breakdown of stable proteins present in sewage sludge when the temperature was above 200 ℃ the partial breakdown of bio-oil into light compounds that are not encapsulated in oil fraction, led to slight reduction in bio-oil yield with a continuous rise in temperature of up to 340 ℃.

c. Effect of Pressure

The partial pressure of gasifying agent in reactor is of crucial importance because it greatly influences the desired yield of product. There is a requirement of optimum partial pressure along with optimum temperature in order to have increased interaction with compounds present in reactor. Additionally, it will be responsible for heating rate thus converting sewage sludge into syngas of high quality [10]. In direct pyrolysis of wet sludge, high moisture content of sludge causes condensation of water which results in increased water content of liquid product leading to various complication in downstream processing and purification of product. On the other hand, high partial pressure of water in reactor in contrast to dry sludge pyrolysis causes an in-situ steam reforming of volatile components which maximize the generation of non-condensable gases after partial gasification of solid char [82]. Therefore, pyrolysis of wet sludge is not suitable for production of liquid fuel.

Furthermore, hydrothermal liquefaction is highly reliant on elevated pressures and temperatures at the critical pressure point where water approaches sub- or super-critical conditions (i.e., near critical region of water) [83]. The density, viscosity, and dielectric constants of water vary dramatically when it moves from normal conditions (20 °C/0.1 MPa) to its critical point (374 °C /22 MPa) [84]. Temperature is the most important element impacting reaction efficiency in sub-critical water, but temperature and pressure both play a role in enhancing conversion efficiency in super-critical water.

In sub- and super-critical states, temperature and pressure may be adjusted to modify the density of water. Due to the low diffusivity of sub-critical water, it has minimal contact with sewage sludge and hence serves primarily as a reaction media [85]. Super-critical water, on the other hand, has a greater diffusivity and speeds up the interaction between the solvent and the sewage sludge. Near-critical water zone, water's hydrogen bonding is weaker therefore, can be used as a hydrogen donor for sewage sludge conversion and as soon it hits the super-critical point, conversion efficiency skyrockets [86]. Free radical reactions predominate in the super-critical area because the likelihood of radical formation from a succession of elemental reaction steps increases as temperature rises [83]. The use of hydrothermal liquefication promote environmental health by converting various forms of sewage sludge to biocrude oil. It has also been employed to remove emerging chemicals [87,88] dichlorination [89] and denitrogenation [90].

d. Action of catalyst

In gasification process, the aim behind catalyst addition is to stimulate the process efficiency followed by degradation of tar contaminants thus producing greater yield of syngas. Tar contains a complex mixture of greater hydrocarbons that needs to be breakdown into hydrocarbons of low molecular weight in gas phase for achieving higher methane, carbon monoxide and hydrogen. In addition, catalyst facilitates mass and heat transfer between the particles in befitting manner. Few catalysts are also added to the reactor as an alternative for sand or as an additive. It also helps in lowering the activation energy thus improving efficacy of gasification and producing higher yields of gaseous products. In addition, Chen et al. [91] studied the effect of Ni-based catalyst on hydrogen gas production through steam gasification of sludge and observed that at 900 ℃, the catalyst loading at a rate of 20 % significantly increased the volume fraction of hydrogen gas by 45.096 %. However, the loading of catalyst at more than or equal to 25 % decreased the yield of produced gas.

Similarly, in catalytic pyrolysis also there is production of liquid fuel with high energy content capable of producing chemicals, power, heat and biofuels. Several studies have stated that addition of a catalyst can significantly enhance the value of end-products. During the process, catalyst can be added at three stages, before pyrolysis, during pyrolysis and after pyrolysis. In many cases, scientists have noticed that catalyst not only increased the bio-oil properties by also improved the hydrogen production followed by removal of chlorine, sulfur and nitrogen. For achieving high yield of fuel, there is a need of optimum reaction conditions for sustainable fuel production. Therefore, the major role of catalyst in pyrolysis is to generate high quality of desired product that can either be bio-fuel, gas or char but in most cases bio-oil is the main desired product [10]. Xie et al. [55] observed that during pyrolysis of sewage sludge, catalyst addition reduced the yield of bio-oil. This might be due to passage of pyrolysis vapours through catalyst particles that enhanced the gas residence time. Therefore, carbonization reactions and thermal cracking of volatiles resulted with great probability, that can decrease the yield of bio-oil and an increment in char yield was noticed upon catalyst addition. However, when the catalyst to feed ratio got enhanced by 1:1 to 2:1, there was an increase in bio-oil yield followed by reduction in gas yield. Hence, keeping in viewpoint the product distribution, catalyst does not enhance the bio-oil yield.

Moreover, in hydrothermal liquefaction several heterogeneous and homogeneous catalysts have shown increased bio-oil yield followed by enhancing through denitrogenation and deoxygenation or both at the same time. Various homogeneous catalysts like H_3PO_4, $FeCl_3$, HCOOH, $FeSO_4$, KOH, NaOH and Na_2CO_3 are widely utilized for HTL and possess a denitrogenation effect. Additionally, the addition of HCOOH significantly enhanced encapsulation of nitrogen in aqueous as well as bio-oil nitrogen [73]. Rahman et al. [34] in their study performed hydrothermal liquefaction of municipal sewage sludge and observed a clear reduction in biocrude yield upon catalyst addition as compared to that in non-catalytic HTL.

e. Effect of particle size

Like all other factors, the particle size of feed also significantly affects the efficiency of thermochemical processes. For instance, a study investigated that liquid yield got increased by decreasing the sludge particles size in fluidised bed reactor. The influence of particle size can be described by distinguishing between rate of heat transfer and intra-particle mass. Small particles on entering the reactor heats up very instantly and rapidly as compared to large particles which undergo slow heating. Additionally, the heating rates of large particles are little uniform, resulting in incomplete fast pyrolysis, thus reduced volatilisation of particles [80]. For instance, Han et al. [92] performed fast pyrolysis of biophysical dried sludge in horizontal fixed bed reactor and analysed the effect of particle size on products yield and syngas composition. The results revealed that large particles (greater than 4 mm) favoured the production of oil with a highest value of around 19 %. In addition, the highest char yield was provided by small particles (greater than 0.27 mm) with a highest value of 60.6% and medium size particles ranging from 0.27 mm to 4 mm favoured syngas production along with inducing greater H_2 and CO emission. In gasification also the feed particle size plays a vital role for achieving high yield of product gas.

Generally, in hydrothermal liquefaction the influence of particle size is very low to negligible. The reason behind this fact is that in super or subcritical water act as an extractant as well as a heat transfer medium. It helps to overcome the flaws of heat transfer thus making particle size a secondary parameter. Therefore, the efficiency of HTL is insensitive to particle size and there is no requirement for extreme reduction in size of biomass feedstock [81]. In addition, Edifor et al. [93] stated that particle size greatly influences the transportation and stability of biosolids slurries preliminary to the production of renewable crude-like oil by hydrothermal liquefaction and the size reduction below 750 μm was regarded as unnecessary. Moreover, Fig. 9 depicts a brief description of different process parameters affecting efficiency of thermochemical methods and yield of bio-fuel.

f. Effect of Heavy metals

Sludge comprises of various heavy metals like zinc, lead, nickel, copper, mercury, cadmium and chromium whose concentration varies from less than 1 ppm to greater than 1000 ppm and they further possess the potential for causing ecotoxicological hazards. The elevated metal content of sludge is regarded to be under investigation and also their fate and mobility is a major matter of concern. In various thermochemical technologies like pyrolysis or gasification, the trace elements are more concentrated in solid or gaseous products. Moreover, studies have also reported on the presence of ketones, esters, carboxylic acids, cyclanes, alkyl aromatic hydrocarbons, halogenated aromatics in the liquid products obtained through pyrolysis of sludge [3]. For instance, Yuan et al. [94] performed the pyrolysis of sewage sludge in a horizontal tubular furnace at 550 ℃ and 850 ℃ for 120 mins and observed the presence of cadmium and zinc in bio-oil obtained at 850 ℃. Hence, the study concluded that high temperature pyrolysis can generate more dangerous bio-oils and moreover bio-oils obtained through low temperature pyrolysis were also risky at different levels. In addition, the need for upgradation or pre-treatment before utilization was also highlighted. Similarly, Tian et al. [95] observed the presence of sulphur and nitrogen content in bio-oil and stated the requirement for extraction so that it can be utilized as fuel.

However, as compared to pyrolysis the chances of gaseous products contamination are more in gasification process due to its high operating temperature which creates a necessity to monitor metal distribution throughout the process [3]. Saveyn et al. [96] performed the gasification of sewage sludge and indicated the presence of heavy metals like zinc, lead and copper in biochar. Similarly, Li et al. [97] evaluate the heavy metals in solid residues from sub and super critical water gasification of sewage sludge and concluded that the total concentration of heavy metals and contamination was increased by two levels after the gasification process. Nonetheless, hydrothermal liquefaction can result in more greener products due to its low operating temperature. As Leng et al. [98] carried out the hydrothermal liquefaction of sewage sludge at 280–360 ℃ and stated that no heavy metals were detected in the gaseous products. In addition, the percentage of heavy metals distribution in obtained bio-oil was less than 10 % but there is no doubt that HTL produce bio-char with high metal content as more than 90 % of heavy metals were distributed in solid char.

5. Technical challenges

Despite of all the advantages, various thermochemical processes like gasification, pyrolysis and hydrothermal liquefaction still faces several challenges that are yet not confronted and needs to be acknowledged further in detail. The key challenges for efficient thermochemical conversion of sludge are as follows:

5.1. Key challenges of pyrolysis or gasification of sludge

5.1.1. Tar issue

At the time of gasification or pyrolysis, generation of tar can be a reason behind tremendous issues like plugging of lines and filters, forming coke etc. leading to significant operational obstructions [99]. This is due to the condensation of hydrocarbon volatiles with molecular weight higher than in benzene [62]. Additionally, tar is also detrimental to human health because it contains various carcinogenic and teratogenic compounds. It further contains consequential amount of energy that can be utilized for gas production. Therefore, generation of tar either in gasification or pyrolysis will not only be responsible for undesirable extent of sustentation for downstream equipment but it will also lessen the energy efficacy of process [4].

5.1.1.1. Catalyst deactivation. Deactivation of catalyst is a very known problem in catalytic methods. It is generally due to active sites poisoning caused by few contaminants present in feed. Another reason behind this is clogging of pores or active sites by coke produced at the time of condensation or cracking of products and reactants. Moreover, in few cases this deactivation might be due to stream washing of metals or chemical variations resulting in loss of active species on surface of catalyst [100]. Likewise, during gasification or pyrolysis of sewage sludge the catalyst may get deactivated due to fly ash produced in process, covering the surface or blocking the pores of catalyst [101]. Moreover, several mechanical reasons like attrition are also responsible for catalyst deactivation. It can be signified by decreased rate of reaction

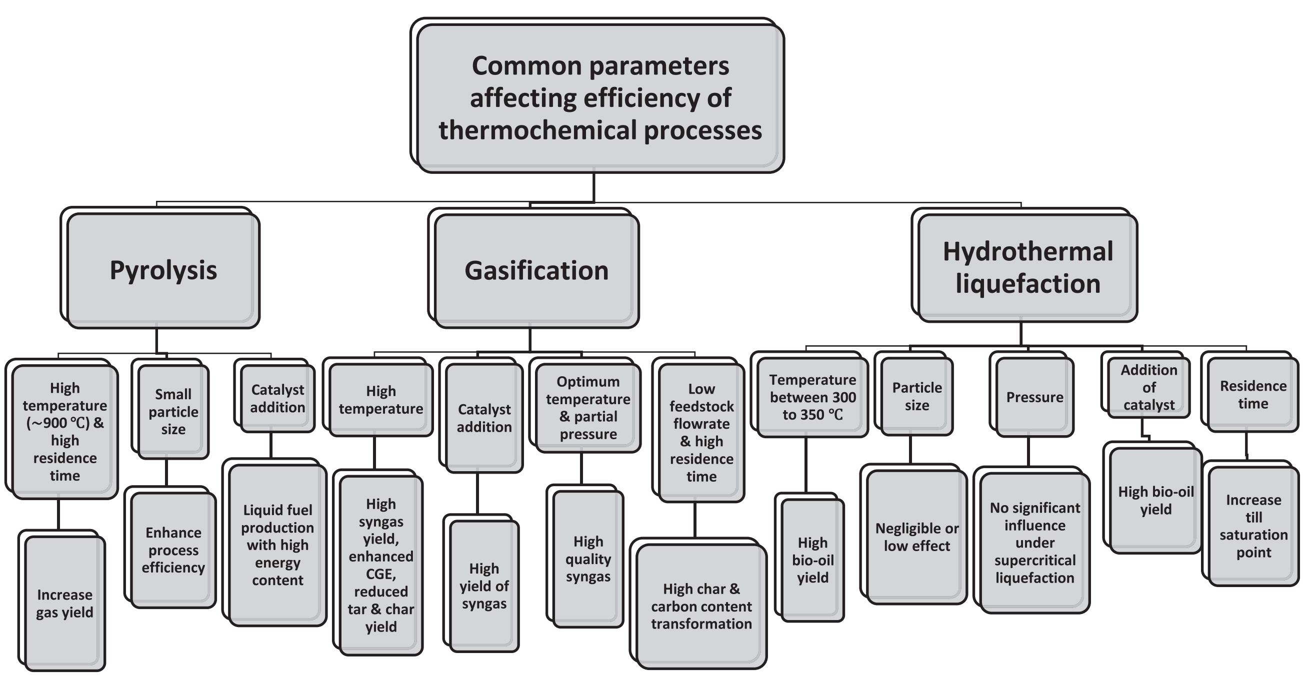

Fig. 9. Common parameters affecting efficiency of thermochemical processes.

and reduced quantity and quality of products [102]. Hence, constant efforts are still required for developing strong catalysts and adequate methods for reactivation, recovery and regeneration of deactivated or used catalysts.

5.1.1.2. High moisture content. High moisture content of sludge can significantly influence the characteristics of generated gas and the gasifier operation followed by high consumption of energy. In addition, the issues can also arise in feeding of sludge into gasifier thus complicating heat and mass transfer due to pasty consistency of sludge with high moisture content [103]. Therefore, drying or dewatering is required prior to gasification or pyrolysis process, which balances the efficacy of energy recovery. However, significant moisture content can upgrade the gasification of biochar and tar decomposition. Moreover, it has been stated that the moisture content limit is dependent on type of gasifier utilized. Anyhow, it is advantageous to consistently maintain the moisture content to less than 30 % for reducing energy losses because of vaporisation and heating of water [104]. Thus, it is mandatory to decrease the water content of sludge to a sustainable limit before feeding it for gasification or pyrolysis treatment.

5.1.1.3. High sulphur and nitrogen content. The significant challenges to gasification of sludge are also bought by high amount sulphur and nitrogen present in sludge which possess a great efficiency for causing secondary environment pollution. At the time of thermochemical conversion, substantial content of sludge-bound sulphur and nitrogen are volatilised at the same time with volatiles during pyrolysis process leading to the production of toxic pollutants like hydrogen sulphide, hydrogen cyanide and ammonia [8]. Moreover, sludge normally constitutes around about 1 wt% sulfur and 9 wt% nitrogen by dry weight, that can emit SO_x and NO_x precursors in gasification or pyrolysis treatment which finally will be responsible for secondary pollution of acid rain and photochemical smog [105,106]. Therefore, to slow down the production of sulfur or nitrogen containing components during gasification or pyrolysis of sludge efforts have been made. For instance, it has been stated that for developing measures to reduce the emissions of NO_x, it is necessary to properly acknowledge sludge-nitrogen nexus at the time of gasification or pyrolysis [4].

5.2. Key challenges of hydrothermal liquefaction of sludge

5.2.1. Catalyst recovery

Although, hydrothermal liquefaction is an efficient technology for thermochemical conversion of sludge to biofuel but still there are some challenges that yet not confronted. Generally, in thermochemical processes the catalysts are employed for enhancing the efficacy of methods followed by reduction in yield of solid residue thus maximizing bio-oil yield. Nonetheless, the recovery of several soluble catalysts from end product, is a challenge that needs energy intensively and expensive separation technologies [107]. Hence, to overcome these challenges, certain heterogeneous catalysts have been tried out that can possibly be reutilized and simply be recovered for many times [108,109]. However, such heterogeneous catalysts are further associated with several challenges like poisoning due to inorganics or tar deposition and deactivation because of metals leaching loss [110].

5.2.2. Continuous v/s batch flow reactor system

During hydrothermal liquefaction, corrosive surroundings are produced by subcritical water that demands the involvement of resistant materials for construction of reactor. Furthermore, due to high pressure and high temperature operating conditions there is requirement of pressure reactors which results in an increased capital cost. Additionally, the produced low solubility compounds easily get deposited in downstream units or reactors that can block the functioning of equipment. Therefore, from the viewpoint of industrial scale applications, hydrothermal liquefaction should be carried out in a continuous flow system possessing higher economic feasibility and efficacy. Nevertheless, hydrothermal liquefaction of sludge is by distant lack of operating experience and commercialized instalment [111].

5.2.3. Product separation

Soon after the process of HTL, acquired products requires separation. On that account, several existing studies have analysed the utilization of organic solvents for extracting bio-oil from solid residues and liquid phase. However, only few studies have focused on studying the effects of such organic solvents on quality and yield of bio-oil products. The addition of organic solvents in HTL process can maximize the overall cost of technique because the solvent requires recovering either by distillation or evaporation where small molecules of bio-oil can be lost by evaporation in addition with solvent, causing deduction in bio-oil yield. Hence, cost and energy efficient separation of bio-oil from hydrothermal liquefaction is still challenging [4].

Moreover, apart from this, some of the other key challenges are as follows:

- Existing studies have focused only on the characterization of bio-oil. However, vital information like heavy metal, volatile content, type and amount of functional group, pH, ash, moisture content etc. is still lacking.
- The commercial trade-offs for bio-oil co-production from biomass by hydrothermal liquefaction should be examined carefully.
- In addition, the information on effect of process parameters, like distribution of particle size, heating rate, size and shape of reactor, liquid–solid ratio, pH etc. is still lacking [28].

6. Recent novel technologies

Besides from all the above discussed influential and novel thermochemical technologies, Supercritical water oxidation (SCWO) and Supercritical water gasification (SCWG) are also few other emerging technologies that are receiving an increased interest of researchers for thermochemical conversion of sludge into bio-oil. The major reason behind this fact is that such technologies also extinguish an energy consuming step i.e., drying of wet feedstock, just like in hydrothermal liquefaction [112]. The water in supercritical state along with coexisting liquid and gas phases can be a source of reactive species engaged for treating biomasses with high moisture content like sewage or additional type of sludge. Under supercritical water, the biomass gasification behaves like an oxidant and O_2 atoms from this state link with carbon atom of feedstock for producing carbon dioxide, which sequentially act with steam for generating carbon dioxide and hydrogen gas by water gas shift. In addition, this method is a better path for hydrogen gas production and is more appropriate for wet feedstock as compared to gasification. However, the production cost of hydrogen gas is higher as compared to that in conventional method [74]. Amrullah and Matsumura [79] performed supercritical water gasification of sewage sludge in a continuous reactor and observed the production of gases involving hydrogen, methane and carbon dioxide. Moreover, a high carbon gas efficiency of 0.73 was achieved at 600 ℃ with 50 s residence time.

Supercritical water oxidation is also an efficient and novel oxidation technology for overall elimination of organic waste. During this process, the organic components and oxidizing agents are completely disintegrated into supercritical water, and homogeneous oxidation reactions are brought out quickly. After a moment or two, organic compounds are extensively modified into harmless substances in the form of minute molecules, like water, carbon dioxide and nitrogen. Simultaneously, heteroatoms are transformed into their equivalent mineral acids or salts depending on the pH of feedstock. This technology removes around 99.9% of organic matters in precisely a couple of minutes. In addition, self-heating balance can also be achieved when a percentage of organic content is greater than 3 wt%. However, supercritical water oxidation further faces some challenges such as problems related to salt deposition, corrosion and high operating costs [113]. Li et al. [114] carried out the supercritical water oxidation of sludge at 520–580 ℃ along with 23–25 MPa of pressure and observed that removal efficiency of organic content was around 99%. Similarly, torrefaction is also a thermal pre-treatment carried out at temperature between 200 and 300 °C in an inert atmosphere. Sometimes, it is also known as mild pyrolysis or roasting and is basically utilized for producing solid product with high energy density, low moisture content, low O/C ratio and high calorific value. This is due to release of H_2O, CO_2, CO and lightweight organic substances. In addition, it can further be coupled with physical densification, drying and torrefaction process [8]. Nonetheless, due to an increased interest in application of hydrothermal technologies more investigations are expected related to sludge thus improving the economic performance and resource recovery.

7. Future perspectives

Thermochemical technologies can be considered as promising in contrast with other conventional methods because they offer certain advantages like recovery of resources and energy, advances in pretreatment, sludge valorisation, intensification of process etc. which are suggested as important factors for sludge. Moreover, to deal with the problems related with disposal and treatment of sludge, there is a need to think out of the box for evolving more innovative and commercialized technologies that will occupy a wide scope in upcoming future. Some of the such innovations can be production of hydrogen gas from sludge, co-gasification, co-HTL and co-pyrolysis of sludge with biomass as discussed below.

- To be particular, catalytic gasification has been considered more promising for mitigation of pollutants, technological evolution, addition of socio-economic advantages, production of environment friendly products etc. because sulfur and nitrogen are found to be highest emitting pollutants from sludge and the utilization of catalyst can be helpful in reducing SO_x and NO_x precursors [10,115].
- Additionally, sludge constitute few distinctive physicochemical properties like low heating value, viscosity, high ash content, high moisture content and density. Therefore, the combination of two processes or materials in a suitable manner can recompense the weaknesses of residues followed by enhanced physicochemical and mechanical properties of new blend material. Nonetheless, few existing studies have focused on the implementation of co-gasification and co-pyrolysis for thermochemical conversion of sludge but still it requires adequate understanding for a wide scope in future [3]. Moreover, Gao et al. [54] also stated that upgradation of bio-oil can be attractive because it reveals properties similar to that of heavy fuel oil but addition of catalyst or co-pyrolysis will be required for that purpose.
- Similarly, hydrothermal co-liquefaction of residues mixture and algal biomass can also be seen as a sustainable modification for selectively adjusting the composition, amount and quality of generated biocrude oil mainly when molecules like sulphur and nitrogen have to meet with specific threshold values for future utilization of biocrude. Hence, few mixtures of residues alone or in combination with algal biomass can be utilized for large scale production of bio-oil with desired quality and yield. Nevertheless, co-liquefaction can be a way for reducing process cost thus ensuring constant and sufficient mixtures of raw material for processing [32,116-119].
- In addition, studies have also shown significant possibility for producing hydrogen gas from wet sludge due to its high moisture content. Wet sludge pyrolysis under high temperature in combination with high heating rates can further increase the generation of hydrogen rich fuel gas [3,120].

8. Conclusion

In recent decades, implementation of thermochemical technologies has been regarded as a promising approach for conversion of sludge into bio-fuel due to several advantages like energy recovery, pathogens inactivation and concurrent volume reduction. They can be a possible route for energy recovery from sludge despite of its heavy metal content, high ash content and moisture content. However, it is concluded that, hydrothermal liquefaction can be considered as the most efficient technology as it has been stated that different products obtained through hydrothermal liquefaction of sludge i.e., bio-char, bio-oil, gaseous phase and aqueous phase possess high concentration of nutrients and organic compounds and moreover the produced gaseous phase is rich in carbon dioxide. Hence, due to these properties, such products reveal a potential for fully utilization [121]. For instance, the solid products can be utilized as activated carbon-based compounds for energy and environmental applications or as soil conditioners. In addition, HTL results in high bio-oil yield in contrast with other methods which has the potential for utilization as fuels in transportation after enhancement and the aqueous phase also possess consequential possibility for carbon sources and nutrients like for algae cultivation. Nonetheless, this provides a clear indication that the HTL process not only holds the efficiency of producing energy but can also yield tremendous advantages related to environment. Furthermore, the direct utilization of aqueous phase for different purposes like anaerobic digestion, catalytic hydrothermal gasification or algae cultivation are also appealing substitutes for production of methane-rich fuel gas and hydrogen-rich fuel gas. Biocrude produced from HTL of sewage sludge can be used as a substitute for fossil fuels. Moreover, as compared to other technologies like pyrolysis, hydrothermal liquefaction does not demand any drying of sludge, hence the wet feedstock like sludge can be liquefied directly that significantly minimize the operational cost of process. Additionally, the biocrude oils obtained through HTL possess higher heating value, low water content and therefore enhanced quality of bio-oils are obtained as compared to those in pyrolysis. Nonetheless, HTL also provides an economically sustainable solution in removing emerging chemical contaminants, denitrogenation and dechlorination.

Although, it offers a potential thermochemical platform, but still further with few technical challenges that requires more work and proper understanding for a better industrialization and commercialization in the market globally. The optimization of process parameters is still needed and vital information about like volatile content, type and amount of functional group etc. is also lacking. Also, use of sludge blends with biomass residues in an appropriate proportion in thermochemical processes appears to be an intriguing prospect that could compensate further shortcomings in order to improve alternative fuel characteristics such as sludge moisture reduction, increased calorific value, and dilution of sludge's undesirable species content.

Nonetheless, the future scope of thermochemical processes can't be questioned for recovery of energy and resources from sludge hence also minimizing its negative impacts on environment and human health.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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