Review

Treatment of Secondary Sludge for Energy Recovery

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ABSTRACT

Primary and secondary sludges are produced as a result of primary and secondary wastewater treatment in municipal wastewater plant or pulp and paper mills. Sludge disposal has become a worldwide problem for many reasons including rapidly shrinking landfill space, increased environmental awareness, more stringent environmental standards governing the disposal of sludge, and dewatering challenges. Unlike the primary sludge, the secondary sludge as byproduct of the biological treatment is far more difficult to dewater and to be disposed. Secondary sludge waste management issues are a continuing challenge. This together with record high oil prices have contributed to a need to examine methods of converting secondary sludge waste into energy. In this chapter, we have overviewed a variety of secondary sludge post treatment methods for energy recovery, including incineration, gasification, pyrolysis, direct liquefaction, supercritical water oxidation (SCWO) and anaerobic digestion. A critical comparison between these methods is presented with respect to their net energy efficiencies. The advantages and drawbacks of each treatment option are also highlighted in this chapter.

CONTENTS

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1. INTRODUCTION

Primary and secondary sludges are produced as a result of primary and secondary wastewater treatment in municipal or industrial wastewater plants, e.g., pulp and paper mills. For instance, about 40-50 kg of sludge (dry)is generated in the production of 1 tonne of paper at a paper mill in North America (Joyce et al., 1979), and of that approximately 70%is primary sludge and 30% secondary sludge (Elliot and Mahmood, 2007). The primary sludge can be relatively easily dewatered for disposal. The secondary sludge consists predominantly of excess biomass produced during the biological process (Ramalho, 1983), and about half of the incoming organic pollution load is converted into secondary sludge, containing 0.5 to 2% solids (Winkler, 1993). Compared with the primary sludge, the secondary sludge is far more difficult to dewater.

The management of municipal and industrial wastewater sludges has been a long-standing challenge for many utilities. For example, Canadian municipalities spend $12–15 billion annually for sewage sludge treatment (Buberoglu and Duguay, 2004). Normally, sludges are disposed by landfilling and incineration (Reid, 1998), which have, however, suffered from their inherent drawback of poor economics due to many reasons including (1) the high cost associated with dewatering the sludge to 20-40% solids or higher so as to meet the requirements of landfilling or incineration, and (2) the significant energy loss in evaporating the sludge-containing water in incineration or combustion of the sludges in a recovery boiler. The sludge disposal/management costs can be as high as 60% of the total wastewater treatment plant operating costs (Canales et al., 1994). In recent years, due to rapidly shrinking landfill space and the secondary pollution issues associated with the conventional sludge disposal approaches as well as the increasingly stringent environmental regulations, the disposal of sludges continues to be one of the major challenges for the municipal wastewater plants and most pulp and paper mills (Mahmood and Elliott, 2006). This together with record high oil prices have contributed to a need to examine methods of converting secondary sludge waste into energy. For instance, the percentage of pulp/paper sludges disposed by landfills has constantly decreased in Europe in recent years, as shown in Fig. 1, dropping 40% in 1990 to 20% in 2002. In the meantime, the percentage of pulp/paper sludge used as a raw material in other industries and other applications (e.g., agriculture as soil improvers, in road construction, land reconstruction) and for energy recovery has steadily increased.

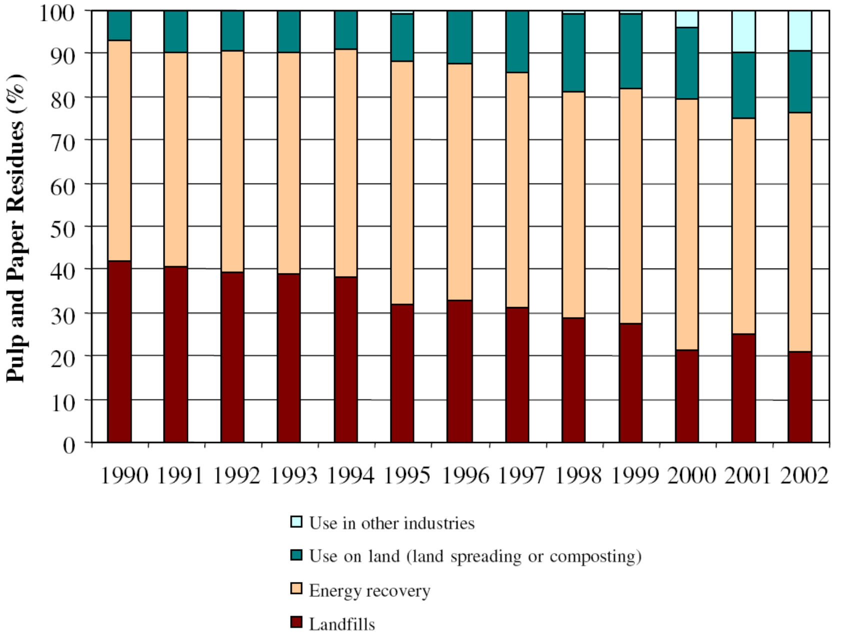


Figure 1. Disposal methods for the pulp and paper residues in Europe (adapted from Monte et al., 2008 and CEPI, 2004)

Comparing with other typical industrial sludges containing 16-35% of total dry solids (Oral et al., 2005; Rato Nunes, et al., 2008), the original secondary sludges from municipal wastewater treatment plant or a pulp and paper mill usually contains a much higher ratio of water (98-99%). A comparison of municipal and pulp and paper secondary sludge characteristics is presented in Table 1. Similarities exist between municipal and pulp and paper waste activated sludge, which would suggest that technologies used in the municipal wastewater sector could be transferred into the pulp and paper industry. General processes and technologies of sludge reduction technologies through process changes (e.g. operational control, and return activated sludge treatment) or through post-treatment (e.g., incineration, carbonization gasification, pyrolysis, supercritical water oxidation (SCWO) and aerobic/anaerobic digestion, etc.) have been recently reviewed by Mahmood & Elliot (2006). While changing/optimizing the sludge producing process would certainly reduce the amount of secondary sludge generation and thus alleviate the issues of sludge waste management, secondary sludge post-treatment technologies and in particular those aimed at energy recovery are the focus of this chapter.

Table 1. Comparison of municipal and pulp and paper activated sludge (modified from Elliott and Mahmood, 2007)

	Municipal	**Pulp/Paper**
Total dry solids (TS) (%)	0.8-1.2	1.0-2.0
Volatile solids (%TS)	59-68	65-97
N (%TS)	2.4-5.0	3.3-7.7
P (%TS)	0.5-0.7	0.5-2.8
Fe (g/kg_TS)	0	0.33-2.2
PH	6.5-8.0	6.0-7.6
Heating value (MJ/kg_TS)	19-23	22-25

To evaluate different post-treatment options and in order to provide a means of comparison, it is advantageous to compare the energy efficiency for each option if possible. A definition of net energy efficiency may be outlined as follows (Xu and Lancaster, 2008). The net energy efficiency or "Energy Output/Input Ratio" can be defined as the ratio of energy content of the objective products to the energy input to produce it, as show in Eq. (1). For simplification of the discussion, several assumptions may be adopted: (1) Since the feedstock used is waste biomass or waste sludge, it can be considered as the feed of "ZERO" energy value, (2) the heat loss of the reactor or process is negligibly small assuming well insulation and (3) the energy consumption by other auxiliary operations (e.g., feedstock preparation and feeding, products separation and recovery, etc.) may be neglected. From the above assumptions, for many hydrothermal treatment processes for the treatment of sludge, the energy input may be approximated by the energy required to dewater/thicken the sludge from its original TS content (e.g. 1-2% for secondary pulp/paper sludge) to a suitable TS content for the process use (e.g 25% TS or above), and to heat the dewatered sludge from room temperature (T_{rm}) to the specified reaction temperature (T).

$$\text{Energy Output/Input Ratio} = \frac{\sum(\text{HHV of the product})\times(\text{mass of the product})}{(\text{Energy Input})} \qquad (1)$$

The approximate energy efficiency of each process can be estimated by the equation above, while depending on different requirements and characteristics of each process, the energy input calculation may differ method to method and may be difficult to determine due to shortage of experimental data reported.

The objective of this chapter is to provide an overview of different types of post-treatment methods of secondary sludge, i.e., waste activated sludge (WAS), for energy recovery. Emphasis is put on the discussion on the energy efficiency for each process, while advantages and disadvantages of each process are also highlighted. An outline of the many post-treatment options and their primary energy products can be summarized in Figure 2. A description of each treatment method including incineration, gasification, pyrolysis, direct liquefaction, super critical water oxidation and anaerobic digestion follows.

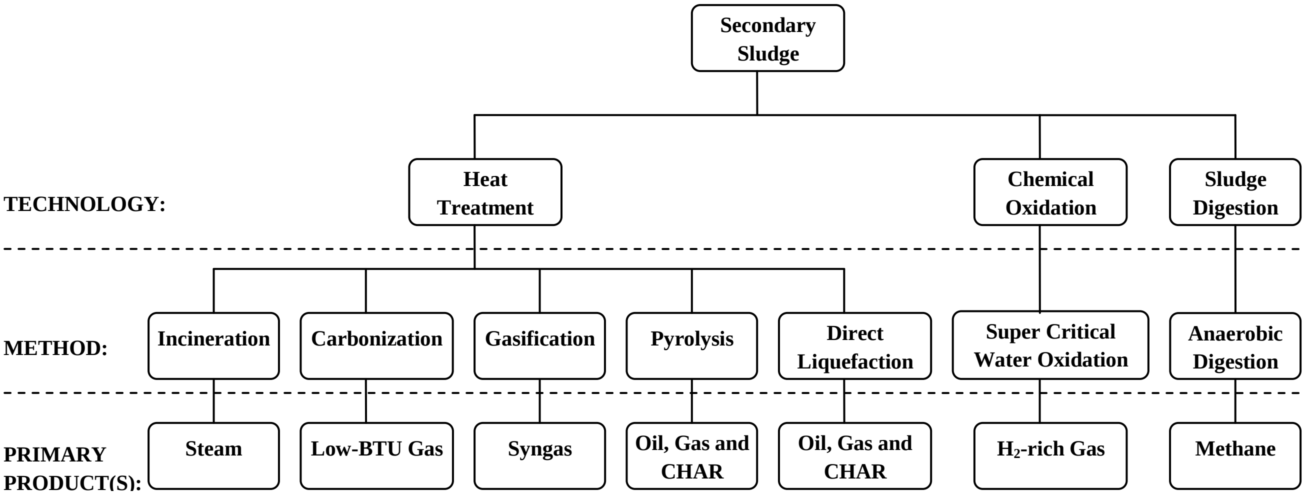


Figure 2. Outline of treatment options of secondary sludge for energy production

2. SECONDARY SLUDGE TREATMENT METHODS

Secondary sludge can be treated by employing a variety of post-treatment technologies such as heat treatment, chemical oxidation and sludge digestion whose processes have been overviewed recently by Mahmood & Elliot (2006).

2.1. Incineration

Incineration technology is the controlled combustion of waste with the recovery of heat to produce steam that in turn produces power through steam turbines (Kumar, 2000). A general flow diagram of the incineration process is depicted in Figure 3. It shows that the sludge is fed into the boiler, which could be rotary kiln, fixed bed furnace or, common in the paper industry, a fluidized-bed incinerator (Latva-Somppi et al., 1997). The incinerator yields products of steam and byproducts of ash and flue gas. Ash can be disposed directly into the nearest landfill or it can be used as the raw materials of light-weight aggregate and constructional brick in the building industry (Liaw et al., 1998; Monte et al., 2008). The flue gas requires treatment through air pollution control before discharge through the stack. However, specifically designed fluidized-bed combustors produce fewer pollutants through the flue gas (Kumar, 2000). For power generation the steam is directed through steam turbines, which work to produce power through the electric generator. Alternatively steam can be used locally for process steam reducing the mill's dependence on costly fossil fuels for steam production (Monte et al., 2008). Typical fluidized bed operating temperature is between 700-900^{o}C (Latva-Somppi et al., 1997). While depending on specific waste regulations in Europe 850^{o}C must be achieved for at least 2 seconds, and if hazardous waste with a content of more than 1% of halogenated organic substances, the temperature is raised to 1100^{o}C for 2 seconds in order to reduce the formation of the toxic compounds such as polychlorinated dibenzodioxins (PCDDs) (Monte et al., 2008). Efficient heat and mass transfer in the fluidized bed enables the endothermic fuel drying and devolatilization to occur simultaneously with exothermic combustion of char and volatiles (Latva-Somppi et al., 1997). Incineration of residues (both rejects and sludge), combined with power and steam generation, is one of the most commonly applied disposal methods in Europe (Monte et al., 2008). Sludge incineration is widely practiced on a full-scale basis in many highly populated urban areas such as in Japan and Germany (Stark et al., 2006). A recent review by Monte et al. (2008) cited eleven European pulp mills which burn some portion of pulp sludge in combination with other biomass. Oral et al. (2005a/b) described a three-stage retrofit of an incinerator in the Czech Republic and concluded that the thermal treatment through incineration of sludge for energy recovery is favorable both economically and environmentally.

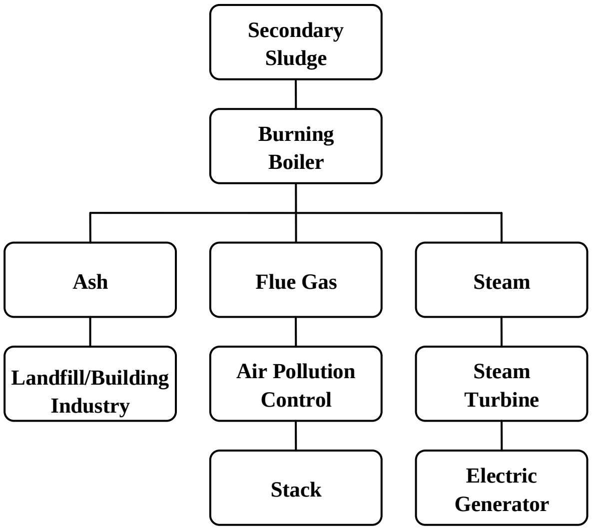


Figure 3. General flow diagram of incineration (modified from Kumar, 2000)

In a sludge incineration process, water in the sludge is completely evaporated and the organic matter in the sludge is effectively oxidized at high temperatures to CO_2 and H_2O, as shown in the following two reactions:

Evaporation: $H_2O\ (l) \rightarrow H_2O\ (g)$
Oxidation and combustion: sludge solids/organics + $O_2 \rightarrow CO_2 + H_2O$ + ash + heat

Since the water evaporation reaction is highly endothermic, in order to sustain the combustion for sludge with a low TS content, dewatering of the original sludge must be conducted or additional fuels (bark, wood waste and oil, etc.) shall be added (Monte et al., 2008). Monte et al. (2008) illustrated that self-supporting incineration (combustion) can be attained for feedstock containing approximately > 25% combustible/organic content and an ash content of 0-60%, where additional fuels are not necessary. Evaporation, oxidation and combustion occur simultaneously. The energy required for evaporation can be estimated using an equation from Kim and Parker (2008):

$$Q_{\text{drying}} = M_{\text{ws}} \times W \times [(C_{\text{p,water}} \times \Delta T) + \Delta H_{\text{vap}}] + [M_{\text{ws}} \times (1-W)] \times C_{\text{p,sludge}} \times \Delta T \qquad (2)$$

Where M_{ws} is unit mass of wet sludge using a basis of 1kg, W is the water fraction in sludge, ΔH_{vap} is latent heat for vaporization of water (2090 kJ/kg), $C_{\text{p,water}}$ is heat capacity of water (4.186 kJ/kg/^{o}C), $C_{\text{p,sludge}}$ is heat capacity of solids in sludge (1.95 kJ/kg/^{o}C) and ΔT is temperature difference between initial temperature of 25^{o}C and the temperature of drying of 105^{o}C. This results in an approximate energy input for drying of 2198 kJ/kg. Further energy input is required to raise the temperature of the sludge from drying temperature of 105^{o}C to an average reactor temperature of 800^{o}C. The further energy input can be estimated at 2753 kJ per kg of the sludge with 10% total solids (TS). An estimated energy consumption of the evaporation energy input plus the energy required for heating the feedstock to the reactor temperature is thus approximately 5000 kJ/kg. Approximately 30% of the solids remain in the ash (Fytili and Zabaniotou, 2008), therefore 70% is combusted. Energy output of the incinerator may be estimated given the steam generation data for the incinerator.

2.2. Pyrolysis

Pyrolysis is a thermal decomposition process in the absent of oxygen to convert biomass or waste materials into solid charcoal, water, water-soluble organics (pyroligneous acids, including methanol and acetic acid); water-insoluble organics grouped under the term of “tar” or “bio-oil”, and non-condensable gases (H_2, CH_4, CO, CO_2**)**.

The chemistry of pyrolysis mainly associates with degradation of carbohydrate polymers (cellulose and hemi-cellulose) and conversion of carbohydrate components, which may be illustrated in Figure 4.

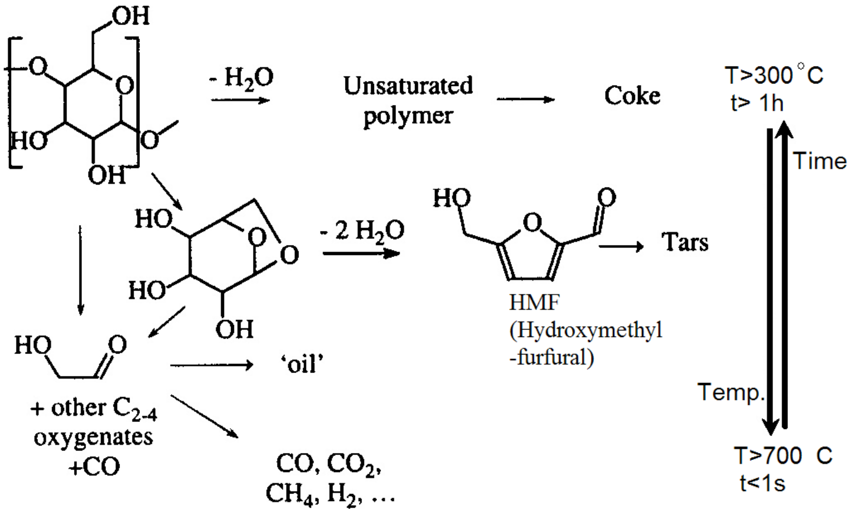


Figure 4. Chemistry of biomass pyrolysis (Lange, 2007)

When heated at a temperature higher than 300°C, the carbohydrate polymers de-polymerize into short chains of sugars, accompanied by slow dehydration and subsequent reactions to form unsaturated polymer intermediates that may be eventually condensed to form char (Lomax et al., 1991). When heated at a higher heating rate to a higher temperature, the de-polymerization reactions will liberate volatile products as oil or tar. Cleavage of C-C bond will occur at a high temperature, leading to formation of gas products (mainly CO, CO_2, H_2 and CH_4). Accordingly, pyrolysis process can be tuned to produce char, oil and/or gas by properly selection of the operating conditions of temperature, heating rate and reaction time. If the purpose is to maximize the oil yield then a high heating rate and short gas residence time would be required, while for high char production, a low temperature and low heating rate would be preferred. High yield of bio-oil up to about 70-75% (Agblevor et al., 1995) can be produced in fast pyrolysis processes (with very short residence time and elevated reactor temperature of ~500°C or higher). The commonly used reactors for fast pyrolysis include bubbling fluidized bed, circulating fluidized bed, ablative, entrained flow, rotating cone reactors, and vacuum reactors (Mohan et al., 2006). A significant amount of char and equal amounts of oil and gas products can be obtained in slow pyrolysis processes (operating at a low temperature for a long residence time). The char produced typically has a higher heating value of ~ 30 MJ/kg, which can be used as a valuable fuel for generating heat and electricity, or can be turned into activated carbon by activation. Pyrolysis oils are normally composed of a variety of organic oxygenates and polymeric carbohydrate and lignin fragments derived from the thermal cracking of cellulose, hemi-cellulose and lignin components of the biomass (Mohan et al., 2006; Tsai et al., 2007). The physical properties of wood fast-pyrolysis oil are compared with those of a petroleum-based heavy fuel oil in Table 2 (Czernik and Bridgewater, 2004). As shown in this Table, pyrolysis oil contains a high concentration of water (15-30%), and is highly acidic (corrosive) and unstable liquid with a lower caloric value of 16-19 MJ/kg compared with 40 MJ/kg for the petroleum-based heavy oil. Pyrolysis oil is a potential liquid fuel for turbines and boilers, or it can also be applied to produce chemicals directly, or be upgraded to high-quality fuels by hydro-cracking or catalytic cracking (Vitolo et al., 1999).

Table 2. Typical properties of pyrolysis bio-oil and of a petroleum-based heavy fuel oil (Czernik and Bridgewater, 2004).

Physical property	Bio-oil	Heavy fuel oil
Moisture content (wt %)	15-30	0.1
pH	2.5	-
Specific gravity	1.2	0.94
Elemental composition (wt %)		
C	54-58	85
H	5.5-7.0	11
O	35-40	1.0
N	0-0.2	0.3

ash	0-0.2	0.1
HHV (MJ/kg)	16-19	40
Viscosity (at 50 ^{o}C, cP)	40-100	180

Pyrolysis has long been recognised more advantageous over conventional incineration processes for the treatment of sewage-sludge with respect to fuel economy, energy recovery, and the control of heavy-metal emissions (Lewis, 1975). However, process efficiency is affected by sludge moisture content, such that co-pyrolysis with other wastes has been recommended in order to increase the dry-solids content of the sludge (Olexseyr, 1975). The process normally needs additional treatment to remove excess water. Higher water content feedstocks cause increases in the production of hydrogen and methane, but these do not compensate for the losses of carbon monoxide and thermal efficiency (Carre, et al., 1989). Water reduction is accomplished by dewatering to about 25% DS followed by thermal drying to 95% DS.

Low temperature pyrolysis with reactor temperature <500^{o}C has also been widely adopted for the treatment of sewage sludge in order to promote the oil yields and to minimize heavy metal evaporation. For a pyrolysis temperature maintained between 500 and 600°C, heavy metals in the sludge (except mercury and cadmium) could be safely retained within the solid chars (Kistler and Widmedz, 1987; Karayildirim et al., 2006). Cadmium has a lower evaporation temperature than most other metals and is dispersed into the gas phase at about 60°C, but can be condensed in gas-cleaning and scrubbing equipment with relative ease, while mercury can be completely evaporated at temperatures above 350°C and is difficult to eliminate from the gas stream (Furness et al., 2000). As an extension of standard pyrolysis, an oil-from-sludge (OFS) process has been developed with the system arranged to maximise the production of high quality oil, which can be used as a fuel (Bridle and Hertle, 1998). In the OFS process, pre-dried sludge (25% DS) is heated to 450°C for a heating period of about 30 minutes under anoxic conditions and at a pressure just above atmospheric, until about 50% of the sludge is evaporated. The vapours are then contacted with residual tar to catalyze the formation of high caloric value hydrocarbons. The process can produce 200-300 litres of oil per tonne of dried sludge. In comparison with incineration and anaerobic digestion, 95-98% of the energy in the dried sludge is recovered in the various products, and the net energy efficiency could be greater. However, the energy input for pyrolysis, including energy consumption for thickening, drying, and heating of the sludge feedstock to necessitate the pyrolysis process, is still fairly high. While the data of energy consumption for thickening of the sludge is unavailable, the energy consumption required to dry thickened waste activated sludge (TWAS) containing about 10% TS to a dry sludge at 105°C is about 2220 kJ/kg-ws, according to Kim and Parker (2008). This is a significant portion of the energy consumption for pyrolysis. Kim and Parker (2008) also found the energy consumption for increase of temperature of the dry sludge from 105^{o}C to reach target reactor temperature of 500^{o}C to be about 770 kJ per kg, while the energy consumed during pyrolysis they assumed to be 300 kJ/kg. Thus, the total energy consumption for pyrolysis at 500^{o}C is 3290 kJ/kg. Energy outputs for pyrolysis include the amounts and heating values of the oil, gas and char products, which is not easy to estimate. Using data from Kim and Parker (2008), the average yields of oil, gas and char were used as 25%, 10% and 65%, respectively, based on dry sludge (or 2.5%, 1% and 6.5% yield of oil, gas and char, respectively, based on TWAS). Average calorific values in kJ/kg of oil, gas and char were used and are 22,500, 1400, and 16,500 respectively. The total energy output is thus estimated to be 1649 kJ/kg. The net energy efficiency, calculated using Eq.1 is determined to be about 0.5, suggesting that pyrolysis is still an energy inefficient process. This conclusion may be supported by the work of Fytili and Zabaniotou (2008), which shows that pyrolysis is a rather endothermic process, of a magnitude of 100 kJ per kg of dry sludge.

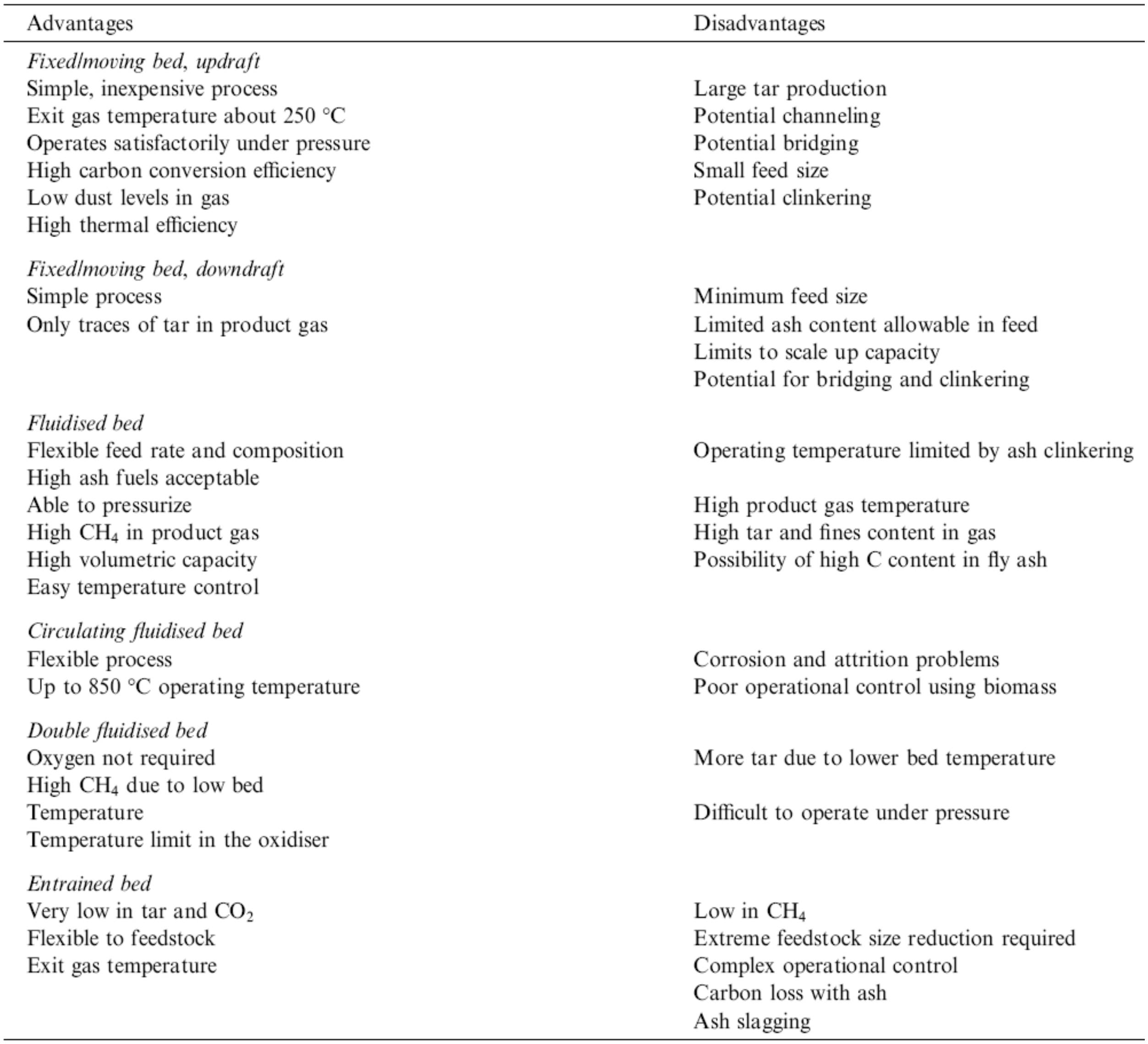
2.3. Gasification

Gasification is a thermo-chemical process during which carbonaceous content of coal, biomass or lignocellulosic wastes is converted to a combustible gas at a high temperature (as high as 900-1400°C) into combustible gases (e.g. H_2, CO, CO_4, and CH_4) in the presence of air, O_2 or steam (Fytili and Zabaniotou, 2008). Gasification technology has been widely used around the world for the production of a fuel gas (or producer gas) from coal and biomass. Typical producer gas from an air-blown gasification process has the following compositions: 9 vol% H_2, 14 vol% CO, 20 vol% CO_2, 7 vol% CH_4, and 50 vol% N_2, with a calorific value of 5.4 MJ/Nm^3 (Furness et al., 2000). As a comparison, an O_2-blown gasification process produces a gas of the following compositions: 32 vol% H_2, 48 vol% CO, 15 vol% CO_2, 2 vol% CH_4, and 3 vol% N_2, with an increased calorific value of 10.4 MJ/Nm^3 (Furness et al., 2000).

Biomass gasification technology has received increased interest in the last decade since it offers several advantages over direct combustion, such as reduced CO_2 emission, compact equipment with small footprint, accurate combustion control, and high thermal efficiency (Rezaiyan and Cheremisinoff, 2005). Gasification technology if integrated with combined cycle gas turbine system has an overall thermal efficiency of 70-80% and an electrical efficiency as high as 50%, offering better perspectives for power generation from biomass (IEA Bioenergy Executive Committee, 2007). It has been shown that biomass gasification plants can be as economical as conventional coal-fired power plants (Badin and Kirschner, 1998). Gasification, in particular larger scale circulating fluidized bed (CFB) concepts, also offers excellent possibilities for co-firing schemes. The gas product of gasification, also known as producer gas or syngas, can be mainly used for steam or heat generation as the fuel gas, for hydrogen and substitute natural gas production, for fuel cell feed, and for the synthesis of liquid fuels such as methanol and F-T liquid through various gas-to-liquid catalytic conversion processes (Dry, 1999). Gasification of biomass has been achieved with various types of gasifiers, ranging from fixed-bed to fluidized-bed and entrained bed gasifiers, whose advantages and disadvantages are as summarized by Rampling and Gill (1993) in Table 3. As revealed in the Table, the major technical challenge for biomass (as well as for sludge) gasification is associated with ash slagging and the formation and removal of tar (high molecular-weight hydrocarbons rich in benzene, toluene and xylene). The presence of tar in the producer gas is undesirable not only because it is an indicator of low gasification efficiency, but also due to the fact that it increases the difficulty of syngas cleanup by fouling and plugging the pipes and tubes of some equipment (Rezaiyan and Cheremisinoff, 2005). It is thus necessary to develop technical approaches to eliminate tar. Tar removal can be achieved either by primary method taking place insider the gasifier or by secondary treatments outside the gasifier (e.g., hot gas cleanup). As a primary method, choosing the proper configuration of a gasifier can reduce tar formation. Brandt and Larsen (2000) produced a significantly low tar formation by employing a novel two-stage gasifier composed of a pyrolysis unit and a gasification unit with a charcoal bed. Nunes et al. (2007) also observed a reduction in tar formation when the producer gas went through a second-stage bed packed with char in a downdraft fixed-bed gasifier. Addition of catalysts, such as char, alkali/alkaline earth metal-based catalysts (e.g. Na, K, and Ca) and transitional metal-based catalyst (e.g., Ni and Fe), proved to be an effective means to reduce tar formation by converting tar into combustible gases through steam reforming, CO_2 reforming, thermal cracking, hydro-reforming/hydro-cracking, and water-gas reactions (Kimura et al, 2006). As the secondary method for tar removal, hot gas cleanup has attracted increasing attention in recent years due to the development of integrated gasification combined cycle (IGCC) and integrated gasification fuel cell (IGFC) technologies. Hot gas cleanup, i.e., catalytic destruction of tarry products and NH_3 (a contaminant species in the producer gas) at a high temperature is needed to further increase the overall power generation efficiency of IGCC and IGFC. The most common catalysts for the decomposition of tar and NH_3 are dolomite (a calcium magnesium ore, $CaMg(CO_3)_2$) and Ni-, Mo-, or Ru-based catalysts (Dayton, 2002), as well as inexpensive Fe catalysts (such as chars from low rank coals with inherent Fe and Ca cations and limonite iron ore) (Ohtsuka et al., 2004; Xu et al., 2005).

Recent developments in biomass gasification including some non-conventional gasification processes are under investigation, such as plasma gasification and supercritical water gasification. Plasma gasification is a gasification process that decomposes biomass into basic components, such as hydrogen, carbon monoxide, and carbon dioxide in an oxygen-starved environment, with the assistance of a plasma torch heating the biomass feedstock to a temperature of 3000°C or higher (Rezaiyan and Cheremisinoff, 2005). This plasma technique has high destruction and reduction efficiencies, and it has great application potential for a wide range of hazardous waste treatment, including both organic and inorganic compounds.

Table 3. Comparison of different types of gasifiers (Rampling and Gill, 1993).



Advantages	Disadvantages
Fixed/moving bed, updraft	
Simple, inexpensive process	Large tar production
Exit gas temperature about 250 °C	Potential channeling
Operates satisfactorily under pressure	Potential bridging
High carbon conversion efficiency	Small feed size
Low dust levels in gas	Potential clinkering
High thermal efficiency	
Fixed/moving bed, downdraft	
Simple process	Minimum feed size
Only traces of tar in product gas	Limited ash content allowable in feed
	Limits to scale up capacity
	Potential for bridging and clinkering
Fluidised bed	
Flexible feed rate and composition	Operating temperature limited by ash clinkering
High ash fuels acceptable	
Able to pressurize	High product gas temperature
High CH_4 in product gas	High tar and fines content in gas
High volumetric capacity	Possibility of high C content in fly ash
Easy temperature control	
Circulating fluidised bed	
Flexible process	Corrosion and attrition problems
Up to 850 °C operating temperature	Poor operational control using biomass
Double fluidised bed	
Oxygen not required	More tar due to lower bed temperature
High CH_4 due to low bed	
Temperature	Difficult to operate under pressure
Temperature limit in the oxidiser	
Entrained bed	
Very low in tar and CO_2	Low in CH_4
Flexible to feedstock	Extreme feedstock size reduction required
Exit gas temperature	Complex operational control
	Carbon loss with ash
	Ash slagging

Recently, supercritical water (SCW), highly compressed water at above its critical temperature of 374°C and critical pressure of 22 MPa, has been chosen as an ideal gasification medium for biomass or lignocellulosic waste conversion primarily because of its special properties such as liquid-like density and gas-like diffusivity. More importantly, SCW has strong solubility for organic compounds, accompanied with its high reactivity (Akiya and Savage, 2002). A wide range of biomass including some model compounds and lignocellulosic wastes have been successfully gasified in supercritical water (Xu and Antal, 1998; Yoshida et al., 2004; Hao et al, 2005; Williams and Onwudili, 2006). Compared to conventional gasification processes, supercritical water gasification (SCWG) has higher gasification efficiency, hydrogen yield and less tar formation (Xu and Antal, 1998). In addition, supercritical water gasification can utilize the wet biomass and wastes directly, eliminating the energy- and capital-intensive drying process. Thus, SCWG is particularly suitable for gasifying biomass with high moisture content and some waste streams such as sewage sludge (Xu and Antal, 1998). A recent study by Izumizaki et al. (2005) summarized experiments where hydrogen was produced from paper sludge in supercritical water in the presence of ruthenium (IV) dioxide, RuO_2. The reaction conditions were 100 mg paper sludge, 20 mg catalyst, temperature of 450°C for 2 hours. The major components of gases produced were hydrogen, methane and carbon dioxide in molar ratios of 27%, 27% and 45%, respectively. One of the author's research group has recently started an extensive study on catalytic gasification of pulp/paper secondary sludge in SCW for hydrogen production. To the best of the authors' knowledge, to date there is no other investigation worldwide that is focused on the use of pulp/paper secondary sludge as feedstock for hydrogen generation.

Energy requirement in different stages of a typical gasification process is outlined in Figure 5, including the location of energy inputs and outputs.

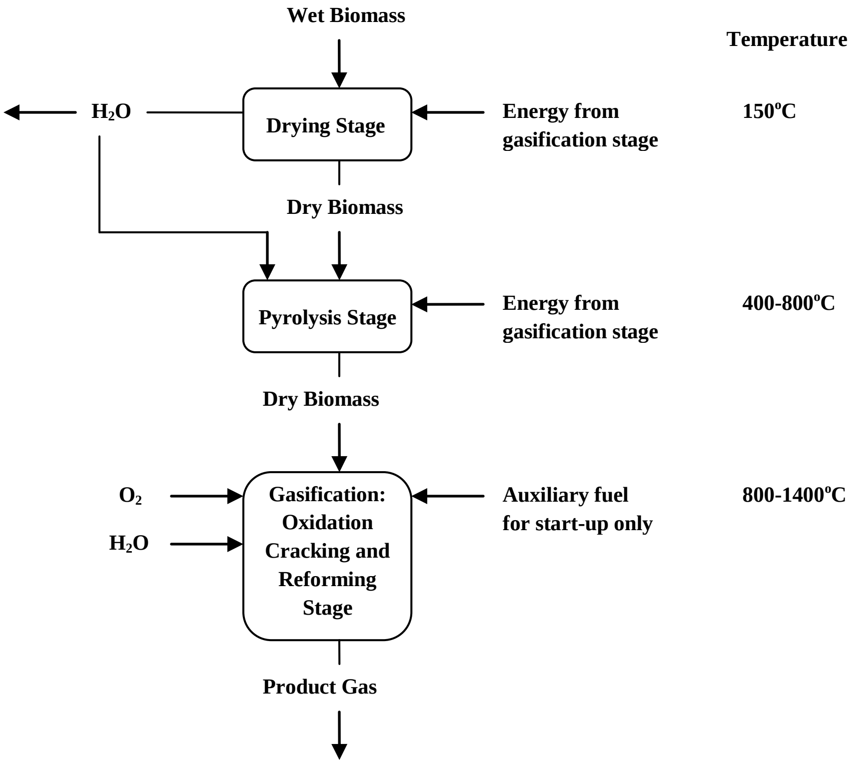


Figure 5. Energy requirement in different stages of a typical gasification process (modified from Furness et al., 2000)

According to Ptasinkski et al. (2007), gasification of raw sludge is not very energy efficient because the raw sludge contains a substantial amount of water (at as high as 98-99 wt%), and hence the optimal reaction conditions are difficult to achieve. In order to improve the gasification efficiency, the moisture content of the sludge must be greatly reduced or dried prior to being fed to a gasifier. According to Kim and Parker (2008), the energy consumption required to dry thickened waste activated sludge (TWAS) containing about 10% TS to a dry sludge at 105°C is about 2220 kJ/kg-ws. It may be possible to use the enthalpy of the producer gas for drying the sludge and biomass feedstock for the gasification. However, the gasification of pulp/paper secondary sludge is a relatively new method and hence not very well documented so far, except for several reports on gasification of a mix of municipal sewage sludge and coal and other domestic waste (Dinkel et al., 1991; Baumgartel, 1993). For dry sludge, the gasification technology has shown to be an energy efficient process. For instance, Hamilton (1998) reported that gasification of dried sewage sludge thermally with the Lurgi-Rhurgas process based on a circulating fluidized bed produced 0.7 m^3 of fuel gas per kg of dry sludge (DS), and the calorific value of the gas was as high as 22.7 MJ/m^3, i.e., a total energy output of about 16 MJ//kg-DS. With dry sludge used, the total process can thus be energetically self-sustaining (Furness et al., 2000).

2.4. Direct Liquefaction

Due to the skyrocketed oil price and the increased concerns over greenhouse gas emissions, there is a worldwide resurgence of interest in the production of liquid oil products (e.g., bio-oils and bio-crude) from biomass through liquefaction. Fast pyrolysis, as described in the preceding section, is so far the only industrially realized technology for bio-oil production (with a liquid yield of 50-70%) (Onay and Kockar, 2006; Maschio et al., 1992). However, the oil product in fast pyrolysis (i.e., bio-oil) consists of a high content of water (20-25%) and oxygen, and hence a low heating value (<20 MJ/kg, about only half of that of crude oil), and the oil is highly corrosive due to its low pH value, as given in Table 2. Without further upgrading, the pyrolysis oil is not regarded as an ideal liquid fuel for heat and power generation. The main purpose of liquefaction is to produce oil products of increased H/C ratios and decreased O/C ratios, and hence a high caloric value relative to those present in the feedstock. Liquefaction can be accomplished indirectly or directly. For indirect liquefaction, biomass is converted into liquid products through first gasification to syngas followed by catalytic conversion (Dry, 1999). Direct liquefaction of biomass feedstocks into liquid oils has attracted more intensive interest, due to its simpler technical route and better conversion economy and efficiency relative to the indirect liquefaction processes. In a typical direct liquefaction process, biomass is converted to liquid products directly but through a complex sequence of processes involving solvolysis, depolymerization, decarboxylation, dehydration and hydrogenolysis/hydrogenation (when hydrogen is present in liquefaction). Direct liquefaction is a low-temperature, high-pressure conversion in the liquid phase, usually with a high hydrogen partial pressure and a catalyst to enhance the rate of reaction (Furness et al., 2000). Yields of the products depend on temperature, residence time, initial biomass concentration, catalysts and liquefaction atmosphere (inert, N_2 or reducing, H_2). The effects on the liquefaction product yields were investigated.

Research on direct liquefaction has been widely performed in the 1980’s for the purpose of alternative energy production (Kranich, 1984; Beckman and Elliot, 1985; Boocock and Sherman, 1985). For instance, in an early study on liquefaction of sewage sludge, conducted by Kranich (1984), sewage sludges were converted to oils in a reaction medium of water or oil at 295-450°C with the presence of a reducing gas (hydrogen) and catalysts of Na_2CO_3, $NiCO_3$ and Na_2MnO_4. The organic conversion rates varied from 45% to 99% and the oil yields were from 35% to 63% in the reaction medium of oil. However, the oil yields were found very low with the water medium (usually less than 20%). Many successful studies on direct liquefaction of biomass in organic solvents such as anthracene oil (Appel et al., 1996; Crofcheck et al., 2005) and alcohols (Miller at al., 1999; Xu and Etcheverry, 2007) have been reported. Hot compressed water and sub-/supercritical water (at temperatures of 200-400°C) are however more advantageous for being used as the solvent in biomass direct liquefaction in that water is likely the most “green” and environmentally benign solvent. Extensive research work has been conducted on direct liquefaction of biomass in sub- and near-critical water. A pioneer work was reported by Appell et al. (1971), where a variety of lignocellulosic materials were efficiently converted to oily products in water at around 350^{o}C in the presence of Co and Na_2CO_3 as the catalysts. Minowa et al. (1998a, b) obtained heavy oil (HO) (with calorific values of around 30MJ/kg) at a yield of 21-36 wt% from a variety of biomass feedstocks in water at 300^{o}C and around 10 MPa with Na_2CO_3 as catalyst. Qu et al. (2003) obtained liquid organic products at a total yield of 30-35% by direct liquefaction of *Cunninghamia lanceolata* in water at 280-360°C for 10-30 min. It has also been demonstrated by Suzuki et al. (1986) that the treatment of sewage sludge by direct liquefaction in water at around 300°C could be a profitable alternative means for sludge disposal. However, the feedstocks tested so far were mainly wood and municipal sewage sludge, and to the best of the authors' knowledge, other than the published work by Xu and Lancaster (2008), no work has been reported on treatment of pulp/paper secondary sludge in hot-compressed water or sub-/supercritical water. As a result, liquefaction as a treatment method is still in the research stages but could potentially be an effective approach to recover energy from the secondary sludge waste for production of liquid oil products.

Xu and Lancaster (2008) experimentally treated secondary pulp/paper sludge in hot-compressed or sub-/supercritical water at a temperature of 250-380°C in order to produce liquid oils for energy recovery from the secondary pulp/paper sludge. An outline of a direct liquefaction process for the treatment of sludge is pictured in Figure 6, where sludge is fed into a pressure reactor where liquid products are primarily produced and gas products are collected. Liquid products are a mixture of water-soluble oil (WSO) and heavy oils (HO) and solid residue or char. Filtration is performed on the liquid product mixture in order to separate the liquid oil products from the solid residue, char.

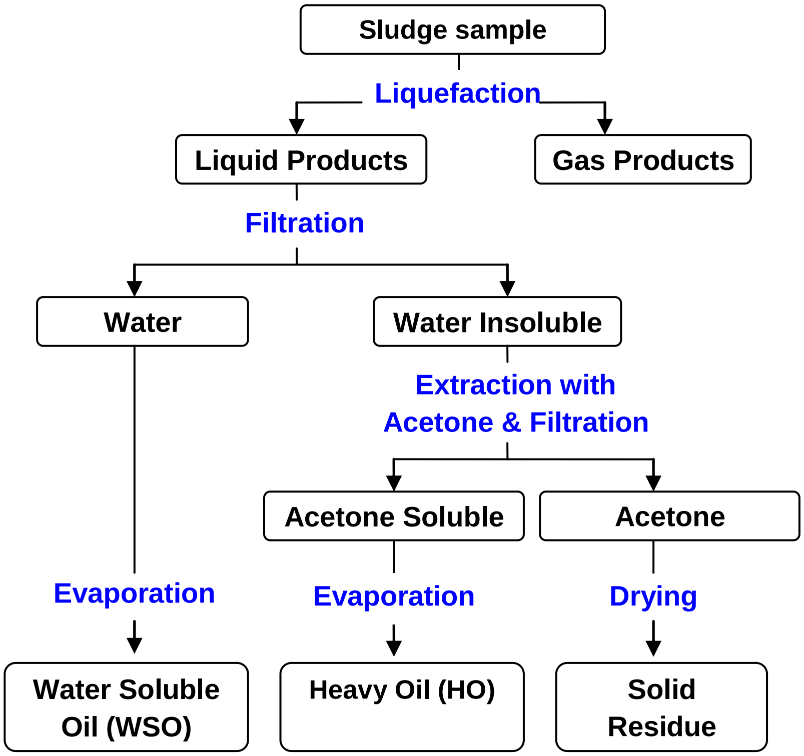


Figure 6. Outline of the direct liquefaction process (adapted from Xu and Lancaster, 2008)

The effects of liquefaction temperature, residence time, initial biomass concentration, catalysts and liquefaction atmosphere (inert, N_2 or reducing, H_2) on the liquefaction product yields were investigated. Treatments of secondary pulp/paper sludge in water at 250-380°C for 15-120 min in the presence of N_2 atmosphere resulted in yields of water soluble oils (WSOs) at 20 wt% - 45 wt% and yields of heavy oils (HOs) at 15 wt% – 25 wt%, with HHVs of 10-15 MJ/kg and >35 MJ/kg, respectively. For temperatures lower than 350°C, as temperature increased the yield of heavy oil (HO) increased at the expense of the water-soluble oil (WSO) formation, while as temperature increased further to above 350°C, the yield of HO decreased, accompanied by an increase in the yield of WSO. An increased residence time produced a greater yield of HO (reaching as high as 25wt% for 120min) but a lower yield of water-soluble and a reduced yield of total oil. A higher initial biomass concentration produced a greater yield of HO but a reduced yield of WSO, while resulting in negligible change in the formation of total oil products. The presence of 0.1M K_2CO_3 dramatically enhanced organic conversion leading to a low yield of char, while the use of the K_2CO_3 suppressed the formation of both types of oils. The use of the two alkaline earth metals catalysts, i.e., $Ca(OH)_2$ and $Ba(OH)_2$, did not alter biomass conversion significantly, but catalyzed the formation of WSO and produced much higher yields of total oil products. The liquefaction atmosphere (inert or reducing) was found to be another important factor influencing the liquefaction process. As shown in Figure 7, it was demonstrated that the reducing atmosphere (i.e., H_2) in the liquefaction process promoted the HO formation while suppressing the WSO formation. With the presence of 0.1M $Ca(OH)_2$ and 2MPa H_2, liquefaction of the sludge powder in water at 280°C for 60 min produced a high yield of HO (26 wt%), almost two times as high as that in N_2 (13.6 wt%), and it produced total oily products (HO+WSO) at a yield as high as 60 wt%.

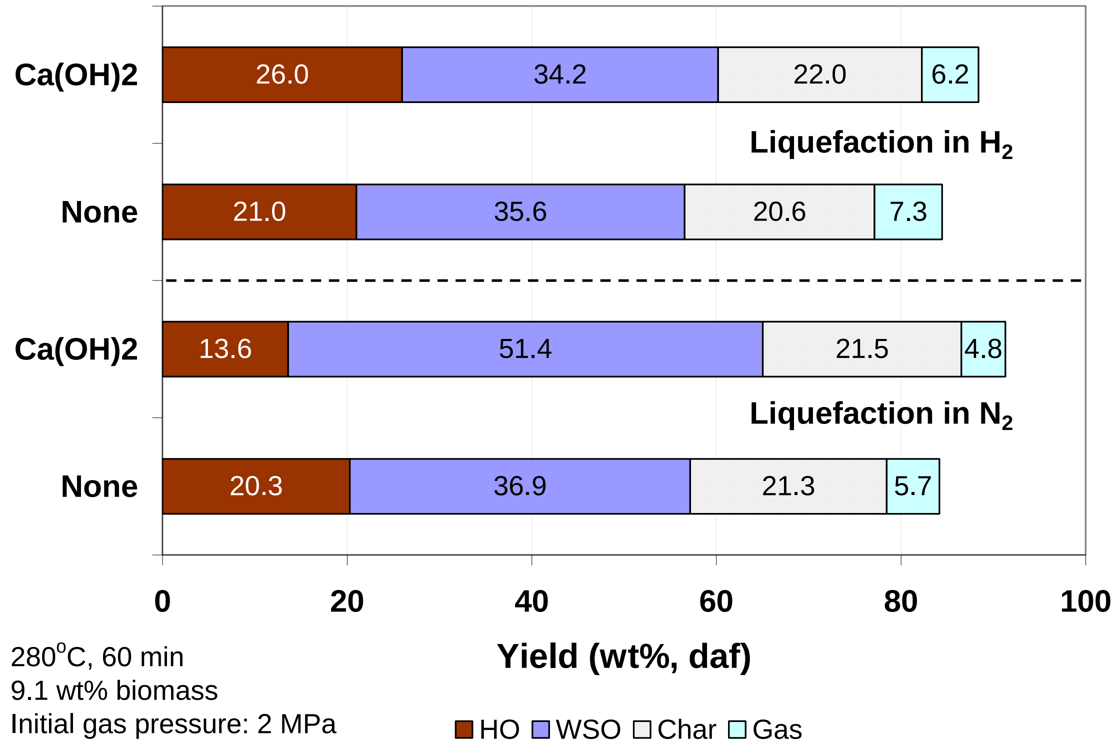


Figure 7. Variation in the product yields with different liquefaction atmospheres (N_2 and H_2) (adapted from Xu and Lancaster, 2008).

In Xu and Lancaster's (2008) work, the energy output/input ratios, calculated based on Eq. (1), were all <1.0, suggesting that the liquefaction operation tested, in a batch reactor, was energy inefficient. However, the energy efficiency can be improved by employing a flow-type reactor and installing a heat exchanger to pre-heat the reactor feed stream using the hot product stream as well as by combusting the resulting chars/gases to provide a portion of the heat for the process. Liquefaction of sludge in H_2, irrespective as to whether a catalyst was present or not, resulted in significantly improved net energy efficiencies. However, the operation in H_2 with the presence of $Ca(OH)_2$ catalyst dramatically enhanced the efficiency to as high as 0.76.

2.5. Supercritical Water Oxidation (SCWO)

Supercritical Water Oxidation, SCWO, also referred to as hydrothermal oxidation, is a process that oxidizes organic solutes in an aqueous medium using oxygen/air or hydrogen peroxide as oxidants, at temperatures and pressures above the critical point of water, i.e., 374^{o}C and 22MPa, respectively (Bermejo et al., 2006). The SCWO process has been under development since the early 1980's when the well known process of wet oxidation was developed at MIT (Modell, 1982). SCW is a superior reaction medium with a high diffusivity, a low viscosity, and relatively high-density therefore rapid oxidation reactions are expected. Moreover, the low temperature of the SCWO process in comparison to conventional combustion can lead to a greatly reduced NOx and SO_2 formation. In addition, water is not only the reaction medium but it participates directly in the reaction through the formation of free radicals (Griffith and Raymond, 2002). Since water is utilized in the reaction there is no requirement to dewater the sludge before processing. Sludge can be processed at 10% solids by weight or even less (Mahmood and Elliott, 2006).

Figure 8 outlines a schematic of a SCWO process. Pressurized sludge (25.5MPa) and pressurized oxygen are fed into the preheater reactor at 25 degrees Celsius. In the preheater the mixture of sludge and oxygen are heated up to approximately 300 to 400^{o}C, to achieve the supercritical state of water. Water at its supercritical state can dissolve organics and hydrolyze even polymers and hence prevent the formation of char (Perry and Green 1999; Fang and Koziński, 2000; Mahmood and Elliot, 2006). The reaction mixture enters the main reactor where the remaining portion of the organics is oxidized in short hydraulic residence time of 5-10 min at the maximum process temperature of around 600^{o}C (Mahmood and Elliott, 2006). After reaction, the effluent is cooled and energy is recovered. According to Svanstrom et al. (2004), about half of the heating value of the sludge can be recovered in the studied process. The solid and liquid products are separated and the wet inorganic solids can be sent to a landfill or spread on dedicated land while the water can be redirected to the wastewater treatment plant.

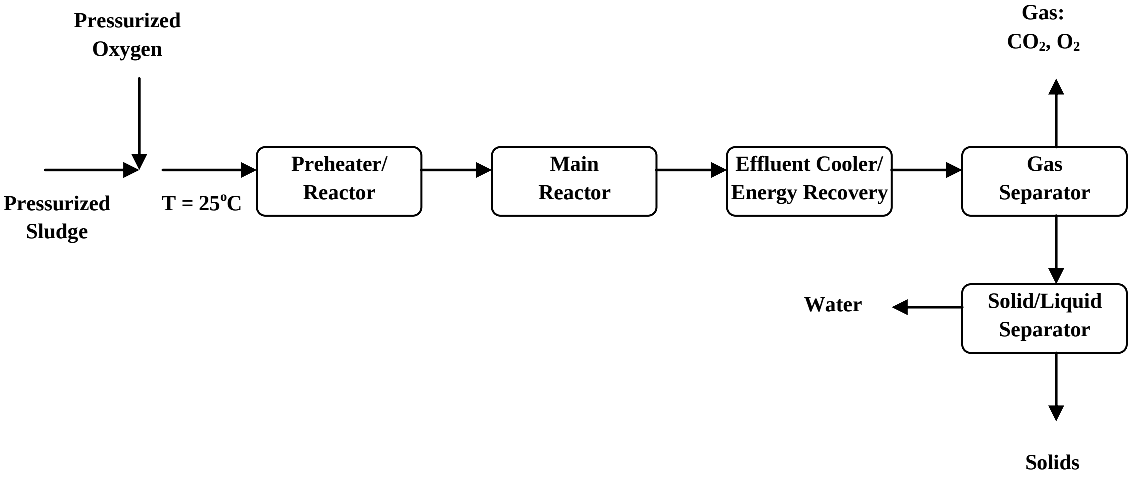


Figure 8. Schematic of a SCWO system (modified from Mahmood and Elliott, 2006).

The effectiveness of SCWO has been demonstrated at the laboratory and pilot scale with a wide broad range of feedsctocks, such as pig manure (Rulkenes et al., 1989), a variety of biomass slurries including pulp mill sludge (Modell, 1990), and sewage sludge (General Atomics, 1997). It has been demonstrated that complete oxidation of virtually any organic material, including hazardous wastes such as hexachlorobenzene, could be achieved by SCWO. A supercritical water oxidation sludge processing plant has been installed at Harlingen, Texas to process up to 9.8 dry tonnes per day of municipal sludge (Griffith and Raymond, 2002). An environmental assessment was conducted on the Harlingen plant and found large environmental gains from recovery of heat thereby reducing natural gas consumption for heat generation (Svanström et al., 2004). Hydrothermal oxidation, in particular SCWO, is currently being considered by various research and waste management organizations as an alternative treatment option (Stark et al., 2006).

2.6. Anaerobic Digestion

Since a large number of the enteric bacteria and viral pathogens presented in untreated sewage are associated with wastewater solids, many are not completely removed during sewage treatment processes and are merely transferred to wastewater sludge (Farrah and Bitton, 1983). Anaerobic digestion processes are widely recognized as particularly suitable for highly polluted wastewater treatment and for the stabilization of primary and secondary sludges. Anaerobic digestion occurs in the absence of oxygen while in the presence of bacterial activity, producing bio-gas (mainly methane). The methane gas produced can be used to generate power by fueling a biogas engine connected to an electric generator. The digested and separated solids can undergo further processing and potentially be used as a fertilizer or soil conditioner for land application (Kumar, 2000; Gavala et al., 2003), while the treated water may be used for irrigation (Kumar, 2000). Anaerobic digestion of municipal or pulp/paper bio-solids could reduce solid wastes by 30-70% with the benefit of energy recovery through methane production. Generally about half of the organic matter in sludge is susceptible to anaerobic biodegradation into the formation of biogas (Elliot and Mahmood, 2007).

The microbiology of anaerobic digestion is complicated and involves several bacterial groups forming a complex interdependent food web. However, four major steps can be distinguished. In the first hydrolysis step, both solubilization of insoluble particulate matter and biological decomposition of organic polymers to monomer or dimmers take place. Acidogensis and acetogenesis follow in the second and third step while in the fourth and final step methane is produced by menthanogenic archaea (Gavala et al., 2003). Figure 9 outlines a flow diagram of anaerobic digestion of secondary sewage sludge for energy production. Secondary sludge is fed into the hydrolysis tank. In conventional single-stage anaerobic digestion processes, hydrolysis is regarded as the rate-limiting step in the degradation of complex organic compounds, such as sewage sludge. Two-stage systems have been proposed to enhance this process (Ponsá et al., 2008). The first stage digests the solids, and the second stage separates the undigested solids from the liquid to form carbon dioxide, methane and water. There are two typical operating temperatures for anaerobic digesters determined by the desired species of methanogens. For mesophilic processes, the optimum operating temperature is 37^{o}C, while 55^{o}C is desirable for thermophilic processes (Song et al., 2004). Thermophilic anaerobic digestion is generally more efficient in terms of organic matter removal and methane production than the mesophilic process (Gavala, H.N. et al., 2003).

Telles et al. (2002) evaluated the performance of a slow rate anaerobic digester in treating secondary sewage sludge. The digester was fed by secondary sewage sludge without any previous thickening, having a concentration of volatile suspended solids (VSS) of 24-29 gL^{-1}. The operation of anaerobic digestion at room temperature was stable, with no noticeable scum or foaming problems. The COD reduction in these experiments reached 29, 21 and 45% in the sludge. Anaerobic digestion of Kraft waste activated sludge (or secondary sludge) was tested with a pilot-scale digester for sludge reduction and biogas production (Puhakka et al., 1992). With sludge containing 38% lignin, 40% reduction of the sludge and a biogas production of 0.5 m^3-biogas/kg sludge removed were achieved. In these tests, 13 g NaOH/kg sludge was added to maintain the optimum pH in the system for the maximum sludge reduction efficiency. Fein et al. (1989) reported that the anaerobic digestion process for the treatment of Kraft mill primary sludge could be significantly more economical than the conventional landfilling. Stahl et al. (2004) also reported a pilot trial using anaerobic digestion to pre-treat wastewater and to digest untreated paper mill effluent, which resulted in a much lower amount of organics entering the activated sludge system, thus substantially reducing the quantity of the secondary sludge from the aerobic treatment operation. Anaerobic digestion has been widely adopted for the treatment of municipal sewage sludge before final disposal and it is employed worldwide as the oldest and most important process for sewage sludge stabilization and treatment (Ponsá et al., 2008). While anaerobic digestion is commonly practiced in the municipal sector, it has not gained popularity in the pulp and paper industry mainly because of its long sludge residence time requirement of 20-30 days (Elliot and Mahmood, 2007). There is currently no full-scale anaerobic digestion facility in the pulp and paper sector for the digestion of solid residues. Nevertheless, there is recent technological advancement that potentially can make anaerobic digestion of pulp/paper sludge more feasible by the development and establishment of pretreatment of sludge prior to anaerobic digestion to accelerate the hydrolysis of sludge.

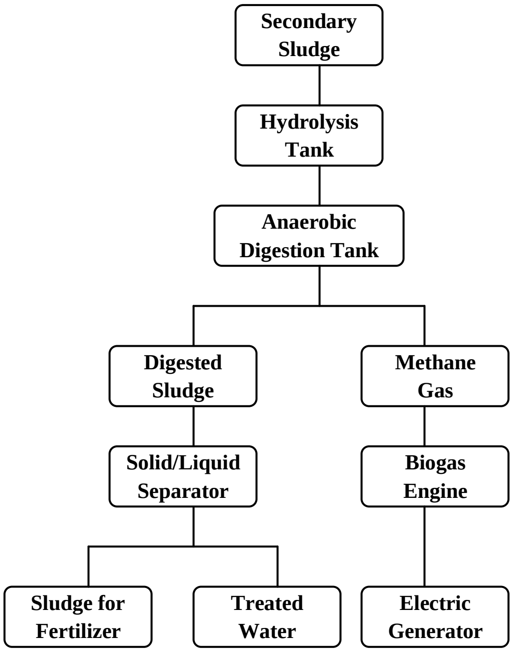


Figure 9 . Flow diagram of anaerobic digestion for power generation (modified from Kumar, 2000)

3. DISCUSSION AND COMPARISON OF TREATMENT METHODS

The operating conditions (temperature, pressure, atmosphere and products, etc.) vary among the methods discussed in the preceding sections, as summarized in Table 4. For example, incineration, gasification and SCWO methods utilize air or oxygen while the remaining methods are conducted under oxygen depleted or anaerobic conditions. Some direct liquefaction processes employ hydrogen gas to obtain better product yields and results. Incineration, pyrolysis and gasification operate at high temperatures, while these methods differ in the objective products. Incineration aims to produce heat and steam/electricity, pyrolysis targets a high yield of oil, and gasification favors production of gas.

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Table 1. Summary of Comparison of Secondary Sludge Treatment Methods

Comparison Parameter	Incineration	Pyrolysis	Gasification	Direct Liquefaction	SCWO	Anaerobic Digestion
Preheating/ Drying required	No	Yes (25% solids, ~150^{o}C)	Yes	No	No	No
Operating Temp (^{o}C)	850-950	400-800	800-1400	250-400	400-600	37 (Mesophilic) 55 (Thermophilic)
Operating Pressure	Ambient	Ambient or slightly above	Ambient	4-20 MPa	22 MPa	Ambient
Operating atmosphere	Air	Oxygen depleted	Air or oxygen	H_2 – reducing N_2 - inert	Air or oxygen	Anaerobic
Primary Energy Products	Steam	Oil, Gas and Char	Syngas	Oil, Gas and Char	Gas	Biogas, Methane

The greatest sludge volume reduction (over 90%) can be achieved with the high-temperature methods including incineration, pyrolysis and gasification, which is advantageous as it effectively reduces the physical amount of sludge for disposal. The major disadvantage for these high-temperature processes is their lower net energy efficiency for the treatment of secondary sludge containing very high content of water (98-99%), resulting from the need of the energy intensive operations of dewatering/thickening and complete evaporation of the water in the sludge. Other main problems concerning these high-temperature thermal processes include excessive energy to reach high temperatures, need for extensive air pollution equipment and, therefore, high capital costs (Monte et al., 2008). In contrast, the other three treatment methods, i.e., direct liquefaction, SCWO and anaerobic digestion, operate at a relatively lower temperature and more importantly without the need of dewatering /thickening and complete evaporation of the water in the sludge. As a matter of fact, for SCWO and direct liquefaction methods, the water in the sludge is the reaction medium and participates directly in the reaction through the formation of free radicals (Griffith and Raymond, 2002). Accordingly, these methods are more promising for the treatment of secondary sludge from the standpoint of energy recovery. A comparison of advantages and disadvantages of different treatment methods are presented in Table 5.

Table 5. Advantages and disadvantages of sludge treatment methods (Kumar, 2000; Furness et al., 2000; Karayildirim et al., 2006; Bermejo et al., 2006; Mahmood and Elliot, 2006; Monte et al., 2008)

Treatment Method	Advantages	Disadvantages
Incineration	- High reduction of sludge volume by about 90% - Nearly complete elimination of the organic materials - Possible utilization for the ashes obtained	- Incineration process can be energy deficient - Air pollution problems (NOx and SO_2 emissions) - Dewatering/thickening of the sludge is required - Emission of chlorinated compounds - High cost due to the increasing demand on the flue gas cleaning
Pyrolysis	- Non-burning process - Production of a mixture of gaseous and liquid fuels and a solid inert residue - Conversion of all sludge biomass fraction into useful energy - Volume reduction by as much as 90% and production of a sterile carbon char	- Dewatering/thickening of the sludge is required. - Less technical maturity for its application to paper/pulp sludges
Gasification	- Higher efficiency of energy recovery - Reduced environmental emissions - Ability to handle most inorganic compounds found in sludge - Production of an inert solid waste	- Dewatering and drying of sludge is needed - Not commercially developed for pulp and paper sludge treatment - Complexity of technology

Direct Liquefaction	- Reaction occurs in aqueous phase, so that no dewatering, thickening and drying of the feedstock is required - Production of a mixture of high calorific value liquid fuels - Conversion of all sludge biomass fraction into useful energy	- Not commercially developed
Supercritical Water Oxidation	- Easily controlled by operator - Reaction medium is water, so no dewatering/drying required - High organic carbon destruction efficiencies	- Corrosion and salt deposition in the equipment which accelerates the deterioration of the reactor
Anaerobic Digestion	- High energy recovery efficiency - Low operating temperature - No dewatering/drying required	- Slow process, long residence times - Cannot accept shock loading and excessive foaming is often a problem

4. CONCLUSIONS

Unlike primary sludge, secondary sludge as a byproduct of biological treatment is far more difficult to dewater and to be disposed. Secondary sludge waste management issues are a big challenge especially with the implementation of more stringent environmental legislation. Typical post-treatment methods for secondary sludges include incineration, pyrolysis, gasification, direct liquefaction, super critical water oxidation and anaerobic digestion. The operating conditions (temperature, pressure, atmosphere and products, etc.) vary among the methods. For example, incineration, gasification and SCWO methods utilize air or oxygen while the remaining methods are conducted under oxygen depleted or anaerobic conditions. Incineration, pyrolysis and gasification operate at high temperatures, while these methods differ in the objective products. Incineration aims to produce heat and steam/electricity, pyrolysis targets a high yield of oil, and gasification favors production of gas. The greatest sludge volume reduction (over 90%) can be achieved with the high-temperature methods including incineration, pyrolysis and gasification, which is advantageous as it effectively reduces the physical amount of sludge for disposal. The major disadvantage for these high-temperature processes is their lower net energy efficiency for the treatment of secondary sludge containing very high content of water (98-99%), resulting from the need of the energy intensive operations of dewatering/thickening and complete evaporation of the water in the sludge. In contrast, the other three treatment methods, i.e., direct liquefaction, SCWO and anaerobic digestion, operate at a relatively lower temperature and more importantly without the need of dewatering /thickening and complete evaporation of the water in the sludge. Accordingly, these methods are more promising for the treatment of secondary sludge from the standpoint of energy recovery.

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