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Thermal pretreatment of municipal solid waste

By

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Abstract

A kinetic study of the pyrolysis of municipal solid waste (MSW) was carried out by thermogravimetric analysis (TGA). Different runs were performed at heating rates of 5, 10 and 15⁰C/min. The effect of the N₂, CO₂ and O₂ gas with different combination in the process was also evaluated. The results show that the most weight loss was obtained when the MSW was treated at a temperature interval of (20-750)⁰C which led to a weigh loss of 95%. The kinetic study of the pyrolysis process showed also the gas mixture used in the process effect also the activation energy of the process and the presence of the CO₂ in the increased the activation energy (Ea) to 56 kJ/mol. Higher concentration of CO₂ in the process lead to increase in the activation energy which is not optimal for the reaction. The treated and the untreated samples were incubated and the biological activity was observed. The results show that the pretreated samples did not have any biological activity. From these results it could be concluded that the thermal pretreatment could be an alternative way for of waste for long period of time, which could have significant impact in i.e. for transportation and durability during storage.

Keywords: Pyrolysis, Pretreatment of MSW, Thermal pretreatment, Thermal gravimetric analysis (TGA)

Executive summary

The reliance on natural resources to boost the economic development has increased. Production and consumption pattern in the past and present have reinforced substantial growth in prosperity in Europe. On the other hand, concern about the sustainability of these patterns regarding primarily the implication linked to use and overuse of these resources together with generation of waste are increasing.

Municipal solid waste (MSW) is an issue that concerns all of us and the definitions varies depending on the country and is collected by, and generally consist of waste discarded at municipal collection facilities from households, commercial activities, office buildings, public institutions, and small businesses. It can be defined as part of or all of household wastes that are collected for recycling and composting, and waste dumped by householders at household waste disposal sites. It can also consist of household hazardous wastes derived from household's street sweepings and litter parks and garden wastes. Proper waste management is the key to ensure resource efficiency and the sustainable development of European economies.

The European Union is making efforts though legislations to reduce the reduce health and environmental impact of waste and at the same time take advantage of the benefits of good waste management, which comprise of the responsibility that individuals, households, businesses and local and national governments have to take. The most important goal is to accomplish much higher levels of recycling or rather avoid waste and use waste as resource where it is possible.

Waste management policies have lately altered the approach to waste management planning from reliance on landfill to Integrated Solid Waste Management (ISWM). In the developing countries in contrast the lack of waste management policies has resulted in the reliance on open dumping. MSW can be a problem if it is disposed however it can represent a great resource that can be beneficially recovered.

Limitations in the amount of waste that is capable to be re-used recycled or composted have made thermal treatment an indispensable option in achieving the targets of landfill diversion. The mean of thermal methods for waste management is to reduce the volume, convert the waste into harmless materials and make use of the energy within the waste as heat, steam, electrical energy or combustible material

There are a variety of systems for collection and transport of household waste such as manual Collection and Vacuum collection systems that are sealed and entirely automated and therefore reduces the unnecessary waste transportation, which in turn is divided in two types, a stationary system and a mobile system. The waste collection in the stationary system is with air in an automated vacuum system and transported via underground tubes. More recent collection system is the Underground container system which is increasing and has the advantage of reduced space on the streets and odor.

During the last decades the import of waste for use in energy recovery has increased. The driving forces for this latest increase of interest of imported waste are the system of infrastructure that permits high energy recovery, high fossil fuel and waste management taxes, high quality of fuels derived from waste in exporting countries, landfilling bans in Europe followed by the lack of waste treatment capacity and differences on gate fee between exporting and importing countries.

The objective of this work was to investigate whether a thermal pretreatment of municipal solid waste could increase the stability of the material and thus lead to better transportation opportunities and at the same time reduce the amount of work needed for handling of municipal solid waste through thermal pretreatment. Part of this work includes an energy analysis to determine how this system would work in large scale.

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1. Introduction

Europe relies a great deal on natural resources to increase its economic development. Production and consumption patterns in the past and present have strengthened considerable growth in prosperity in Europe. Nevertheless, concerns about the sustainability of these patterns are increasing, mainly regarding the implications associated to use of resources and over-use of these resources.

From a life-cycle standpoint on natural resources, several environmental concerns associated to production and consumption, together with the use of resources and the generation of waste is arising. At the same time as both, exploitation of resource and waste generations have different environmental impacts. Both of the issues share several of the same driving forces, which are for the most part related to how and where we produce and consumer goods, and how we use natural capital to maintain economic development and consumption patterns. Use of resource and generation of waste in Europe continue to increase. There are however large national differences in use of recourses per person and waste generation, depending on social and economic conditions as well as different levels of environmental awareness. Resource extraction in Europe has been stable over a decade; however, the reliance on imports is increasing. Waste management has been a center of EU environmental policies for more than 30 years, which increasingly necessitate the reduction, reuse and recycling of waste, and are contributing to close the loop of material use by providing waste derived materials as input for production[1].

It is estimated that, about 1 kg of household waste is produced per citizen and day. In a number of industrialized countries can this value even be twofold. Although, this is the case and the proportion of source separated materials, disposal can be comparable to that of a less developed country. A family consisting of four people produces about (1tonne) of municipal waste per year, which would result in a landfill volume of approximately one cubic meter. With a typical landfill height of 30m, a city of one million populations requires annually (1hectare) for land filling its waste, considering other waste in addition to its household waste. This demonstrates the reason why technical alternative with a high potential to decrease the volume of waste for landfill disposal have been and still is in high demand. For example incineration reduces the volume of waste down up to 15–20% [2].

After separation of some recoverable material at source which is usually considerably lower than 100%, the composition of MSW consist of one third of compostable materials like kitchen waste, one third of combustible materials like plastics, paper, textiles, and one third *inert* for example glass, ceramics, stones and metals. In total there is also another third consisting of water, mostly in the compostable portion [2].

2. Waste definition

The definition of municipal solid waste (MSW) varies, but usually includes waste arising from private households that are collected by local authorities from different sources. MSW therefore consist of a fraction of commercial and non-hazardous industrial waste. The definition can include depending on the country, part of or all of household wastes that are collected, waste collected for recycling and composting, and waste dumped by householders at household waste disposal sites. It also includes household hazardous wastes derived from household's street sweepings and litter parks and garden wastes [3].

Waste is a subject that concerns all of us. It is estimated that on an average, each of the 500 million people living in the EU discard about half a tone of household waste every year. In addition to this waste there are other waste generated from activities like manufacturing (360 million tons) and construction (900 million tons)[4].

In total, the European Union annually generates by about 3 billion tons of waste. This huge amount of waste has an enormous impact on the environment, causing a pollution and greenhouse gas emission that contributes to climate change. Since EU is highly reliant on imported raw materials this would subsequently create a particular problem.

The quantity of waste we are generating is steadily increasing and the nature of waste itself is shifting, partially because of the rise in the use of hi-tech products. Consequently waste now consists of a complex mixture of materials, such as plastics, precious metals and hazardous materials that are difficult to handle safely [4].

EU waste management policies aspire to decrease the environmental and health impact of waste and improve the efficiency Europe's resources. The aim is to turn Europe into a recycling society, avoid waste or using waste as a resource where it is possible. The goal is to attain much higher levels of recycling and to reduce further extraction of natural resources. Proper waste management is a solution to make sure resource efficiency and the sustainable development of European economies[4].

The European Union is making efforts to reduce the negative impacts of waste and at the same time take advantage of the benefits of good waste management, which includes the responsibility that individuals, households, businesses and local and national governments have to take[4].

2.1 Origin and Composition of MSW

Municipal solid waste is collected by, or on the arranged by, the local authorities and generally consists of waste discarded at municipal collection facilities from households, commercial activities, office buildings, public institutions, and small businesses. The definition of "municipal solid waste" could, however, differ from country to country. Rapid growth of cities increase the quantity of waste produced in limited and populated regions. This consequently, might eliminate the possibility of economical methods of disposal. In rural areas, for example crops and animal wastes are growing as pesticides and fertilizers are applied more often. However, a lot of these biodegradable materials could be burned as fuel

or simply converted into a soil conditioner and should not be considered as real waste [5]. Figure 1 illustrates a typical composition of MSW in United Kingdom which could be representative for developed nations [6].

2.1.1 Domestic Waste

Domestic waste is defined as waste raised from household activities, such as food preparation, cleaning, fuel burning, clothes and furniture, old apparatus and equipment, packaging, newsprint, and garden wastes.

In developing countries, domestic waste consists mainly of food waste and ash. In developed countries the proportion of paper, plastic, metal, glass, and hazardous matter is larger [5].

2.1.2 Commercial Waste

Commercial waste is waste from shops, offices, restaurants, hotels, and similar organization or institutions waste collected from these type of commercial establishments usually consist of packaging materials, office materials, and food waste and have a close similarity to domestic waste. Food markets contribute a large proportion of the commercial waste in low-income countries. Commercial waste could contain hazardous components, for instance contaminated packaging materials [5].

2.1.3 Institutional Waste

Institutional waste is waste mainly from schools, hospitals, clinics, government offices, military bases etc. Institutional waste resembles to both domestic and commercial waste, however the proportion of packaging materials is more than food waste. Hospital and clinical waste consist of infectious and hazardous materials. To reduce health risks it is essential to separate the hazardous components from non-hazardous [5].

2.1.4 Industrial Waste

The composition of industrial waste largely depends on the type of industries involved. Industrial waste consist of mainly components similar to domestic and commercial waste, including food wastes from kitchens, packaging materials, plastics, paper, and metal objects. A number of production processes, however, utilize or produce hazardous substances such as chemical or infectious. Disposal methods for hazardous wastes usually vary from non-hazardous waste and also depend on the composition of the waste type [5].

2.1.5 Street Sweepings

This waste largely consist of dust and soil together with different amounts of paper, metal and other waste from the streets. In developing countries, street sweepings also include drain cleanings and domestic waste discarded along the roads, plant remains, and animal manure [5].

2.1.6 Demolition and Construction Waste

The composition of construction and demolition waste depends on the origin of building materials, but usually includes soil, stone, brick, concrete and ceramic materials, wood, packaging materials [5].

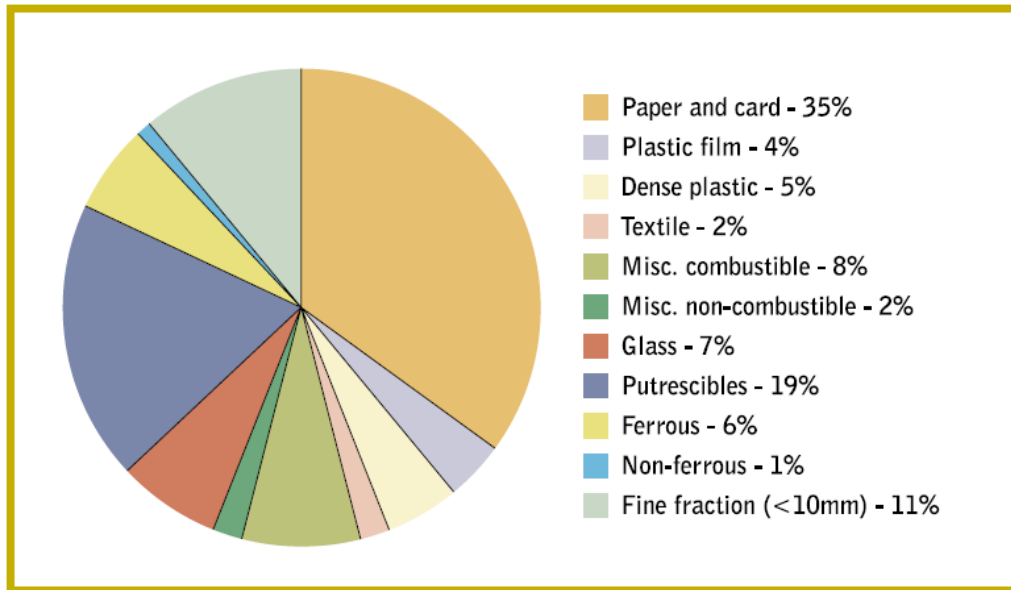


Figure 1. MSW Composition [6].

3. Theory of waste management

Practicing waste management in industrialized countries developed in 1970's with the focus on decreasing environmental impacts of waste which was done by building controlled landfill sites, setting up waste transfer stations or modifying waste collection vehicle route.

In the beginning of 1990's the focus shifted to new technological solutions for waste management and in the mid 1990's focus started gradually to shift towards resource recovery. Due to this new focus recycling, incineration, composting and biological treatment for energy and nutrient recovery techniques are today integrated in municipal solid waste management (MSWM) systems. Waste management policy alterations in recent times have changed the approach to waste management planning from dependence on landfill toward Integrated Solid Waste Management (ISWM). In the developing countries on the other hand the absence of waste management policies has resulted in the reliance on open dumping. World Bank and other agencies have often supported construction of sanitary landfill in these regions [7].

Interest of the environment new directives and legislations in the EU and US on waste disposal are promulgated for example in 2003 Sweden increased the tax to 370 Swedish Kronor per ton of waste landfilled [7] and United States' Resource Conservation and Recovery Act (RCRA) demanded that landfills sites to be impermeably lined and equipped with leachate and gas collection equipment. Such Policies and their enforcement have assist the developed nations in employ the waste hierarchy; prevention, materials recovery, incineration and landfill.

To achieve the objectives of these policies, a verity of model or systems of waste management such as cost benefit analysis (CBA), life cycle analysis LCA and integrated waste management have developed. Waste management systems based on cost benefit analysis

generally translates all economic, social and environmental impact into economical terms for example impacts attained by the cost of building of waste management facilities and the profits generated from it . Estimation of social and environmental impacts are done by the cost of reduction of pollution from a waste treatment facility and/or the extend of the public agreement to compensate for an environmental improvement. These estimations help to make a decision for management options offer the best benefit. Maximization of economical efficiency is generally the main factor in CBA rather than environmental and social reasons, which is not always a sustainable approach towards waste management. Waste management practices that involve life cycle analysis (LCA) of products engage the estimation of the environmental aspects and potential impacts during a product's life from raw material throughout production, use and final disposal. Recently waste management systems are concerned with the entire life cycle of products aiming to make a full evaluation of the environmental impact systems. This approach is fundamentally for waste minimization since it recommends producers, alternative production routes and strategies for waste reduction. Nevertheless, the life cycle analysis is a specific and technical environmental process which cannot deal with social issues such as health effects in an effective way and hence, cannot be considered a sustainable waste management system. The theory of integrated waste management was developed linking the waste streams, waste collection, treatment and disposal methods together with the LCA concept at the same time as aspiring to accomplish environmental benefits, economic optimization and also social acceptability. Municipal waste management should be connected to local environmental, economic and social concern and further to engage the public before any important waste management decisions are made [7].

3.1 Waste handling

MSW can be a problem if it is disposed, however it can represent a great resource that can be beneficially recovered through recycling of materials or through recovery operations such as utilization of the energy content by combustion and composting. However, large quantities of MSW are disposed in landfills mainly because of low cost and ready availability. In landfill the biodegradable components of MSW decompose and cause emission of methane which is a greenhouse gas 23 times worse than carbon dioxide [6] and contributes to significant environmental problems. Other components such as leachate can also cause air and groundwater pollution, and give raise to problems like odour.

Because of these reasons most countries aspire to decrease their reliance on the use of landfills for MSW. EU countries have set ambitious goal for decrease the biodegradable component of MSW send to landfill and increase the MSW subjected to recycling and recovery operation. A number of European countries such as Sweden, Germany and the Netherlands, have already banned the biodegradable fraction from landfills. Numerous developed countries have taking on the principle of the waste hierarchy which gives guidelines for preferable waste management options from the point where the waste arise through to final disposal to facilitate their policies on MSW management as illustrated in figure 2.

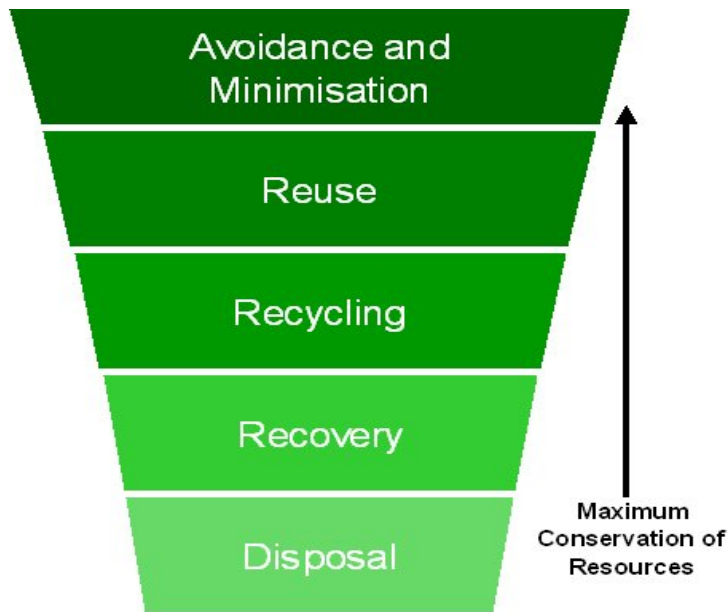


Figure. 2. The Waste Hierarchy (<http://www.wastenet.net.au/information/hierarchy>)

Recycling of materials is preferred to treatment for energy recovery if it is economically possible, and environmentally sound. In reality however, even countries with developed recycling infrastructure, considerable amount of MSW remain after recycling and the most economically viable option is disposal to landfill [6].

Researchers are now focusing on balancing between waste minimization, material recycling, energy recovery and landfill of the non-biodegradable fractions MSW. At the same time as the composition of MSW can be very variable, in particular between developed and developing countries, the elimination of materials for recycling leave a residue that has a considerable calorific (heat) value making it suitable to energy recovery. In general, one tonne of MSW has approximately one-third of the calorific value of coal comparing 8-12 MJ/kg received for MSW and 25-30 MJ/kg for coal, and one tonne of MSW can generate around 600 kWh of electricity [6]. Conventionally, waste mixtures are incinerated in mass burning facilities however, the development with new installations is to elevate efficiencies in power and Combined Heat and Power (CHP) production. A number of countries require a minimum efficiency [6].

3.2 Waste management in Sweden

Management of waste is a vital part of the infrastructure of the society and of the society's utilization of raw material, nutritional substances and energy. With the right waste treatment, it is possible to contribute to preventing climate change and make use of waste as a resource. For example energy recycling during incineration – Waste-to-Energy – provides heating and electricity, and waste will as a result replace fossil fuels and material recycling saves energy and substitute virgin raw materials [8].

In 2009, household waste volumes in Sweden were reduced by 5 percent compared to the year before [8]. Approximately, 1.4 percent went to landfill and even this amount has decreased by 50 percent comparing to 2008. The quantity of treated household waste in 2008 was 511.2 kg/person [8]. Reducing waste volumes is something that Sweden, and all other countries in Europe need to attempt. EU requires through the framework directive for waste that all member states to take actions to avoid the production of waste. The goal is to reduce the waste volume by 2020 and Swedish Waste Management together with the Swedish Environmental Protection Agency is one of the important actors in this process. The aim is to increase awareness of the waste policy in EU and the member states, and illustrate the direct effect of consumption on the environment and on the greenhouse effect. It is also important to highlight the correlation between waste minimization and sustainable development. Swedish Waste Management in the spring of 2008, owing to local authorities' demand of a system which allow comparisons, follow-up and statistics proposed for waste planning which is projected for those that are involved in the waste industry, decision-makers, authorities, educational institutions, media, and other concerned parties [8].

Waste treatment should be employed in such a way that the maximal environmental and social benefits are accomplished. All parts are obligated to participate in this work, from producers to households. The local authorities are responsible for the household waste, the producers are accountable for their different product groups, and the operators are responsible for taking care of all other waste that is not categorized as household waste. The households are responsible to separate and dump waste at the different collection sites and to follow the regulations for waste management in their municipality. Management of waste is followed according to a five step waste hierarchy: waste prevention, reuse, material recycling, recovery and disposal. For economical or environmental reasons there are however some exceptions[8].

3.2.1 *Extended producer responsibility*

The theory of Extended Producer Responsibility (EPR) was officially established in Sweden by Thomas Lindqvist in a 1990 in a report to the Swedish Ministry of the Environment. Extended producer responsibility (EPR), is derived from the "polluter pays" principle, and involve making manufacturers accountable both financially and physically for the whole lifecycle of the products and packaging after their useful life and handle them through reuse, recycling or in energy production, or hand over the task to a third party, which is known as

producer responsibility organization (PRO). These organizations are paid by the producer for the product management. Thus, EPR move responsibility for waste from government to private industry, force manufacturers, importers and traders to integrate the environmental costs of products into the products price. The long term intention of EPR is to promote environmentally friendly and sustainable product development. Products that need less resource are easier to reuse or recycle, and include smaller amount environmentally hazardous substances. The difficulty, subsequently, is to develop flexible EPR-strategies for a future since there is an uncertainty about, national or international directives, technological and industrial developments, changing political ideas, market forces and ethical concern [9].

3.3 Collection and transport of waste

There are a variety of systems for collection and transport of household waste. At the recycling centers, the households can drop off their bulky waste which is too heavy for gathering it in bags or bin like broken furniture, toys, bicycles, electronic waste and hazardous waste[10].

It is estimated that the amount of bulky waste is 161 kg per person and about 600 recycling centers exist in the country and these centers have about 20 million visitors each year [10].

The amounts of bulky waste and hazardous waste handled by recycling centers have increased considerably. In numerous municipalities the recycling centers have, therefore, been adapted and modernized. In order to develop the security and functional system for access control that would facilitate more precise visiting statistics, municipalities have also installed a barrier gate system center, which is combined with an entry card that offers households the right to visit the centers a without charge in a certain number times [10].

The recycling stations contain bins for newspaper and different packaging material. A number of municipalities have also curbside collection which is a small part of collection system, put into service from apartment blocks and separate house properties. This type of collection system is increasing. The household waste in storage bin and bags can be collected both as a mixed fraction that goes to “Waste-to-Energy” treatment or in separate fractions. The most common however is separate collection system or so called source-separation system, there food waste is separated by two different bins where one contain bio-waste and the other contain combustible waste.

Manuel Collection of waste in the past led to many work-related injuries. Nowadays the circumstances are different. New technology and automated systems such as refuse vacuum pipes and underground container systems replaced the old system of heavy manual handling, mainly in big cities [10].

Vacuum collection systems are sealed and entirely automated and therefore reduces the unnecessary waste transportation, particularly in residential areas.

Vacuum collection systems are divided in two types, a stationary system and a mobile system. In the stationary system the waste is collected with air in an automated vacuum system and

transported via underground tubes, up to a distance of two kilometers, which are attached to a big container located in a terminal [10].

The mobile vacuum collection system uses air as well, while, the vacuum technique comes from a mobile vehicle and a storage tank placed under all inputs. The tanks are linked, to a docking point placed 300 meters from the tanks by an underground pipe system. For emptying the vehicle is attached to the docking point. The vacuum system is then switched on and air transfer the waste from the several storage tanks to the docking point and onto the vehicle. Specialized vehicles are required for this type of collection systems [10].

Underground container system is another kind of collection system that is increasing, there are advantages by putting containers underground, the space needed on the streets is reduced, the low temperature underneath the street level, prevents odor, and the containers are without difficulty emptied using a crane truck or a front-loading vehicle [10].

3.4 Import and export of waste

Importing and exporting of waste in European Union, specifically among member states and countries outside the EU, is controlled through the Waste Shipments Regulation. The transported waste for disposal and recovery is mainly divided into three groups mainly categorized on the basis of its content of hazardous components: green (e.g. fire-wood, chips, bark briquettes, powder, tall oil, chemically untreated used wood, sorted fractions of plastics, paper, rubber) , yellow (e.g. chemically treated used wood, mixed fractions of used wood, paper, rubber, plastics, MSW) and red (e.g. wastes containing, consisting of or contaminated with polychlorinated biphenyl (PCB) or polychlorinated dibenzo-dioxin Peroxides other than hydrogen peroxide. If the type of waste belongs to green waste, there is no requirement to report the transported amount. However if the waste is yellow and red type it have to be approved by Swedish Environmental Protection Agency (Swedish EPA).

Between the years 1996 to 2002, the Swedish import of waste for use in energy recovery increased. The waste was predominantly yellow waste, (97–99)% [11]. The import of yellow waste consisted largely of separated wood waste and a mixture of wood, paper and plastics waste, which was combusted in different district heat production plants (DHPPs). Various waste mixtures were imported to incineration plants for energy recovery however this waste was usually a mixture of household waste, which was inhomogeneous and had levels of heavy metals and corrosive substances that were excessively high to be combusted or incinerated in DHPPs. In 2002, 10% of the import of yellow waste was used for energy recovery. The import was primarily transported from Germany, Netherlands, Norway, Denmark and Finland. The driving forces for this latest increase of interest of imported waste are the system of infrastructure that permits high energy recovery, high fossil fuel and waste management taxes, high quality of fuels derived from waste in exporting countries, landfilling bans in Europe followed by the lack of waste treatment capacity and differences on gate fee between exporting and importing countries.

However the prospect shows that the strength of these forces most likely will be decline. The reason for this is that in European countries, the aspiration to reach the Kyoto targets and increase in competition for the production of electricity from renewable sources such as waste derived fuels in contrast with fossil fuels. This would increase the cost of fuels, derived from waste after full implementation of the Waste Incineration Directive [11].

3.5 Waste treatment methods today

There are four important treatment methods for waste, that is, material recycling, biological treatment, Waste-to-Energy and landfill and the local authorities are free to decide management method and municipal activities preferable, separate or combined with other municipalities. Collaboration is also possible in a common committee or a local government federation. For local authorities to collaborate is beneficial in environmental and social point of view, to accomplish cost effective treatment and to assure the competence necessary.

In 73 percent of the Swedish municipalities, external actors and private companies take care of the collection of household waste and the rest; it is handled by the municipalities themselves this is also applied to waste treatment which effected either by the municipalities or by an external actor [8]. The MSW can be treated in different pathways as shown in figure 3.

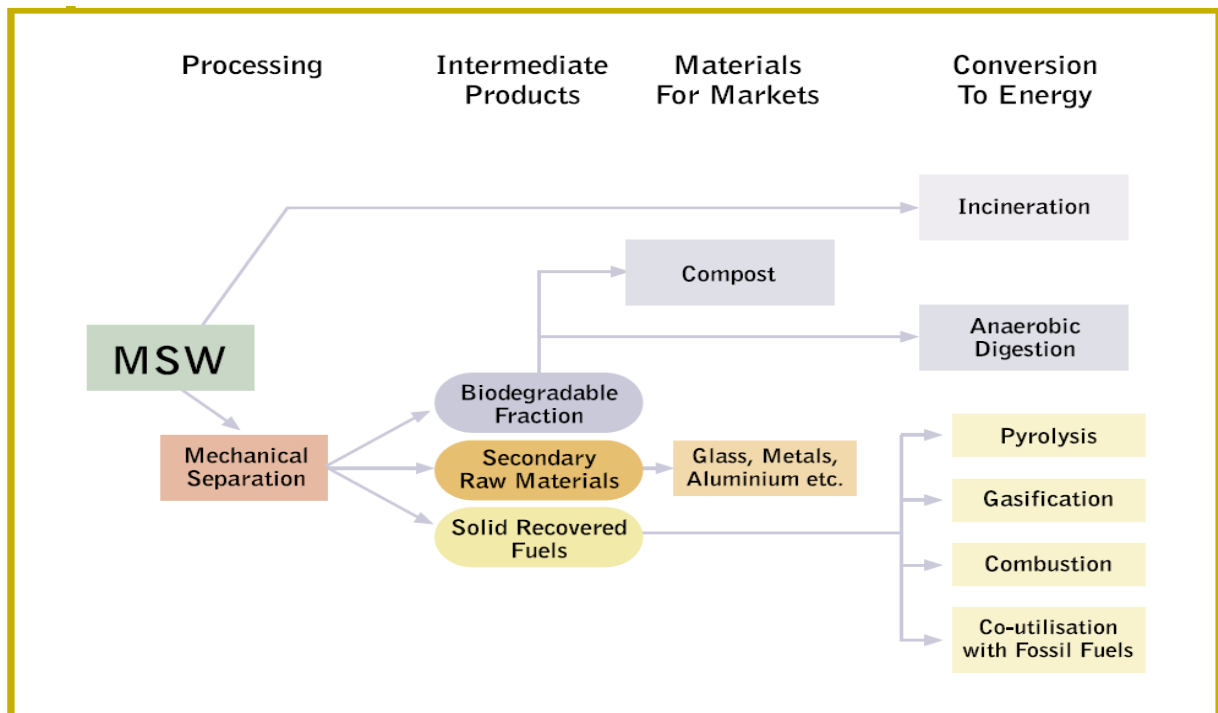


Figure 3. Pathways for MSW treatment processes [6].

3.5.1 *Material recycling*

In 2009, 49.2% of material was recycled including biological treatment. Of all treated household waste the fraction of material recycling that includes packaging, electronic waste, and bulky waste collected, decreased by 35.4%. One reason for the decreased amount of waste that goes to material recycling is the economic recession. Less consumption results in less amount of waste [8].

3.5.2 *Biological treatment*

Investigations shows that every Swedish resident generate close to 100 kg of food waste each year, primarily from fruit and vegetables. The most ordinary system used is source separation. This biological waste is treated either through anaerobic digestion there biogas is produced or composting. Biogas is considered renewable and the most environmentally friendly fuel available, which is used for vehicle fuel, heating and electricity generation [8].

According to calculations of Swedish waste management, 21% of the food waste was biologically treated in 2009 [8].

Approximately 13.8% of all household waste is treated biologically today. This is about 49.2% of household waste which is recovered either by material recycling or by biological treatment [8].

3.5.3 *Waste-to-energy*

Energy is recovered in plants there household waste is not treated. Since the 1980's Sweden has imposed regulations on emissions (air and water) from incineration of waste Most of the emissions have been decreased by 90-99% since then [8]. Other factors, has also contributed to this reduced emission, for example advancement of technological development and enhanced waste separation have contributed to reduced emissions [8].

The remains from incineration comprise of bottom ash, which is about 15-20% by weight of the treated waste, and flue gas treatment residues, which is 3-5 percent by weight [8]. Some fraction of the slag is landfilled, whereas slag gravel is used as an alternative to natural gravel, for instance, in road and landfill construction work. The residues from flue gas treatment can go both to landfill or be used for neutralization when refilling mines. Recently imported waste for utilization in energy recovery has increased. It is estimated that Sweden has imported about 36480 tons of household waste in 2009 [8]. Waste is becoming more and more important source of district heating systems in Sweden. Swedish waste management and the Swedish district heating association estimated that the emission of greenhouse gases has reduced as a result imported waste going to Waste-to-Energy. The most important cause for the reduction of emission is that imports substitute waste treatment in the origin country. This is because of landfilling, which, thanks to import, allow a significant reduction of methane a potent greenhouse gas.

According to some reports comparing to landfilling, transportation of waste only marginally contributes to the greenhouse emissions and even EU Framework Directive for waste, claims that waste incineration with effective energy recovery is considered as recycling. It is a

hygienic and environmentally friendly treatment method of waste that either cannot or should not be treated in other ways.

Waste-to-energy stands for 48.4% of the entire amount of treated household waste. Development and improvement have increased energy recovery in the last years. In 2009, of total, 13.9 TWh of energy produced through incineration 12.3 TWh was used for heating and 1.6 TWh for electricity [8].

3.5.4 Landfill

Landfilling is usually the option if the waste should not or can't be treated by any other methods. In 2009 the amount of waste landfilled in Sweden decreased by 55 percent, compared to 2008 [8]. In 2008, EU regulations concerning landfilling took action, and about half of all landfill locations for municipal waste were shut down. In 2009, only 85 landfills were open. The majority of these sites take just non-hazardous waste, while 21 of them also take hazardous waste. Landfills that are closed are required to be capped with a final cover. Annually, roughly 6-8 million tons of material is applied for the final covers of landfill sites. About 248 GWh was generated from recovered landfill gas at 36 active landfills in 2009, and 11 GWh was used for electricity. Further 35 GWh was flared which just reduces methane emissions Energy is however not produced from flaring [8].

Some of the active landfills have local treatment of leachate which consists of, some type of biological treatment to decrease the nutrient emissions. Modern landfill sites in addition to disposal attend to the waste separation of materials that is sent to treatment or recycling [8].

3.5.5 Environmental impact of MSW management

The combustion of MSW has the benefit of decreasing MSW waste streams, and thereby reducing the creation of new landfills. The combustion of MSW leaves a solid waste called ash. The ash contains any of the components that were originally presented in the waste. MSW power plants decreases the need for landfill capacity since disposal of the ash require less land area comparing to unprocessed MSW. However, because ash and other residues from MSW processes may contain toxic materials, the power plant wastes must be tested frequently to guarantee that the wastes are safely disposed to avoid toxic substances from migrating into ground-water supplies. Under present regulations, MSW ashes have to be sampled and analyzed constantly to determine if it is hazardous or not. Hazardous ash must be controlled and handled as hazardous waste. Non-hazardous ash should be disposed of in a landfill or recycled for use in roads, parking lots, or covering for sanitary landfills depend on local distractions and country [12].

The most important advantage related to energy recovery and all development with renewable energy technologies from MSW is a decrease of the gaseous pollutants that effect the environment. According to a study by IEA the conventional MSW energy recovery systems, such as mass burn the emitted amount of CO₂ is 1100 kg per tonne of MSW and 1833 grams of CO₂ per kWh [6]. Different measurements illustrate that approximately 20-40% of the carbon in MSW is coming from fossil sources, like plastics, depending on the level of separate collection of paper and organic waste. The remaining is derived from biomass and therefore is considered as a renewable resource [6].

Consequently the non-renewable constituent of the emission is around 367 g of CO₂ /kWh (20% of the total emission of 1833 g of CO₂ /kWh) [6]. If, for instance, the MSW was disposed to landfill about (50-100) kg of methane could possibly be released for every tonne of waste. Knowing the high global warming potential of methane, this would be equivalent to 1610 kg CO₂ /tonne of MSW. In current landfills, approximately half of the methane produced can be extracted and used for generation of energy, thus decreasing the total emissions[6].

Additionally, the energy production from MSW stops the emissions associated to release that energy from fossil originated sources which can as a result cause a net reduction of emissions in greenhouse gases [6].

With MSW combustion, there is no degradable organic material dumped in landfill. Materials that embed high energy such as steel and glass could be recovered prior to incineration and for this reason some CO₂ emissions could be avoid (figure 4) [6].

Additionally, the energy generation from MSW avoids the emissions that could be generated from fossil sources. The recovery of energy from MSW can consequently lead to a net reduction in greenhouse gas emissions (Figure 5).

The use of technology for energy recovery from MSW will have local environmental impact connected with traffic movements, noise, and local effects of pollutants; on the other hand these effects could be reduced significantly if best practice in the design, and operation of plant were adopted [6].

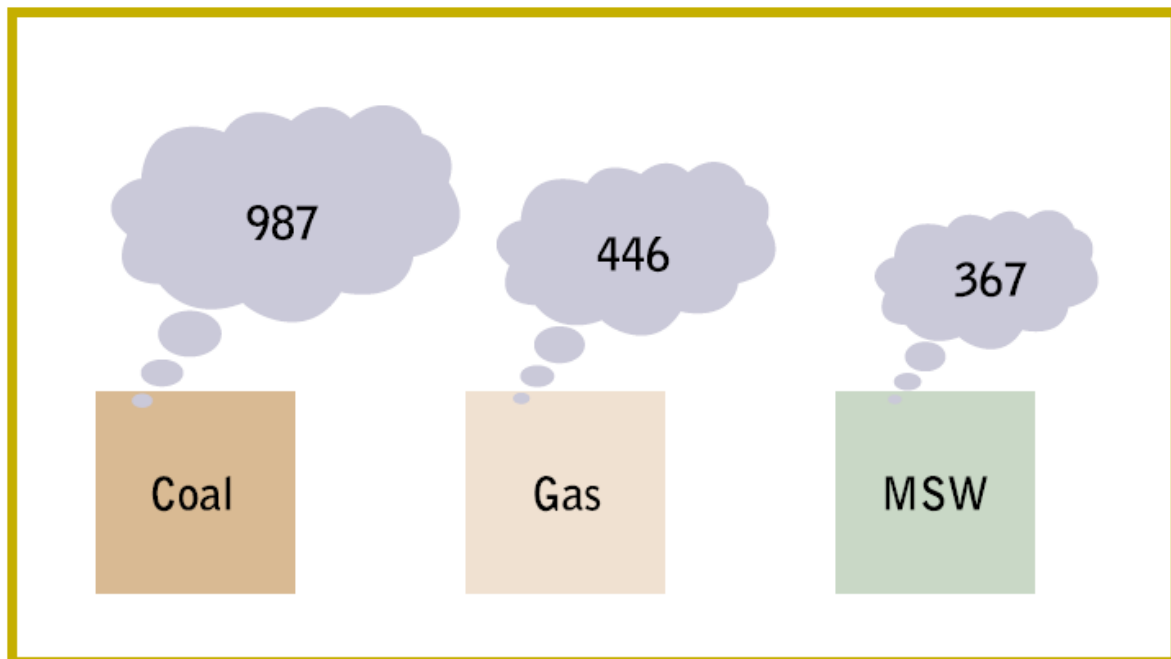


Figure 4. Life Cycle CO₂ emissions– kg per kWh of electricity [6].

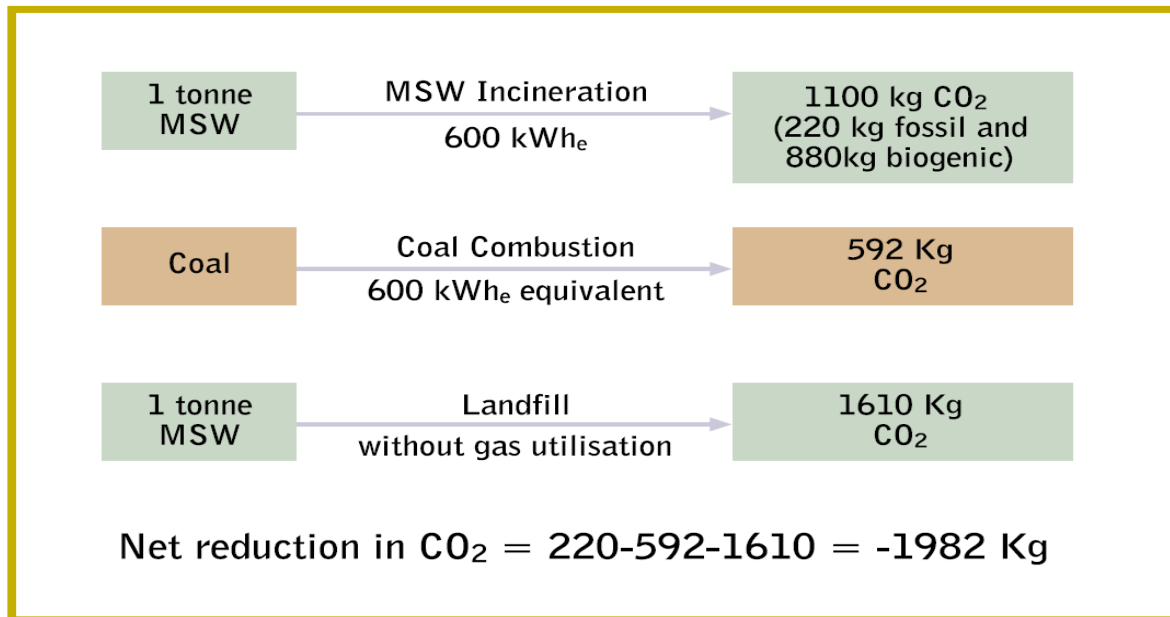


Figure 5. Greenhouse gas emissions from electricity production: MSW incineration compared to coal combustion and landfilling of MSW (kWh = kilowatt hour of electricity) [6].

4. EU legislation on waste management

In 2005, the commission made a proposal for a new directive on waste. The EU's present legislation on waste management is derived from the Waste Framework Directive (WFD), presenting a description of waste and a general ranking of the waste management methods consisting of:

1. Prevention
2. Recovery
3. Incineration through energy recovery
4. Incineration with no energy recovery
5. Disposal

Knowing that not all waste can be prevented or recovered, the EU has in addition implemented directives on waste incineration and landfilling.

The Waste Incineration Directive (No.2000/76/EC) requires that waste incineration facilities shall cover an environmental consent and sets out rules related to operating conditions to air and water emissions. The strict requirements had to be fully fulfilled by incineration facilities in operation by the end of 2005.

The Landfill Directive (No. 1999/31/EC) requires that just the waste that has been subjected to treatment can possibly be landfilled. This however may not be relevant for inert waste since treatment is not technically possible, or to any other waste that such treatment does not contribute to the directives goals. Moreover, the directive demands that the member states shall make arrangements for a strategy for achieving the reduction of biodegradable waste subjected to landfill. Biodegradable waste is preferred to be recycled, composted, material and energy recovered and digested for i.e. biogas production. The strategy should make sure that the quantity of bio-degradable municipal waste aimed for landfill is decreased by 2016 to 35 percent of the amount generated in 1995. The directive proposes several particular requirements for the design of and the approval of waste going to landfills.

In 1989, within the framework of the OECD, the Basel Convention on the Control of Trans boundary Movements of Hazardous Wastes and their Disposal was signed, which was an attempt to stop exports of hazardous waste to developing countries.

The EU has proposed ‘Council Regulation (EEC) No. 259/93’ in 1993, called the waste shipment regulation, on the supervision and control of shipments of waste inside, into and out of the European community, which was altered in 2005. The revised regulation specifies the shipments of waste in and out of the borders must be noticed by the capable authorities in the state of destination [13].

5. Thermal treatment of MSW

The aim of thermal methods for waste management is to reduce the volume, convert the waste into safe materials and utilize the energy within the waste as heat, steam, electrical energy or combustible material [14].

Limitations in the amount of waste that is capable to be re-used, recycled or composted, both practically and financially have made thermal treatment options such as incineration /combustion, pyrolysis, gasification an essential option in achieving the targets of landfill diversion. Pyrolysis and gasification processes have long history in the coal industry but it was recently the search for more efficient energy recovery, has shifted the focus towards development of gasification and pyrolysis technologies for processing MSW [15].

The most important management action that influences waste treatment is the waste generation which means waste minimization will have an effect on both pretreatment techniques and landfill behavior. Every process that modifies the composition or other characteristics of the waste stream subsequent to landfilling is considered a pretreatment technique. Solid waste pretreatment techniques are conventionally connected with mechanical, thermal and biological pre- treatment. These techniques are presently used, most often in combination, with the intention of material recovering, producing energy and reducing the amount of waste designated to landfill. The solid waste pretreatment techniques is mainly affected, aside from economically, by the composition of the waste

Up to 60% of total volume reduction of waste from a municipality might be accomplished through mass burning [16]. This is however largely relying on initial waste composition and

density. The decrease of the MSW organic content by burning, on the other hand, is also expected to effect in considerable reduction of organic landfill emissions. The solid waste that leave a mass burn facility contain bottom ash, fly ash and a variety of other residues from flue gas treatment and recovered material or rejects in preparation of the combustible part. In the US, bottom ash is normally landfilled with no processing, although metals and other materials could be recovered by magnetic separation and screening. The market for such recovered materials is not sufficient to sustain recovery efforts. In Germany, bottom ash is somewhat recycled (about 60%) as a building material (e.g. support layer in roads), while in Switzerland more or less 100% of the generated bottom ash is transported to landfills [16].

The thermal treatment of solid waste is merely one branch of an integrated waste management system. Thermal treatment can be important in an integrated waste management system Figure 6 illustrate how thermal treatment is incorporated in conventional waste management system.

Thermal treatment could:

- I. Decrease the quantity of waste, consequently preserving landfill space. However thermal treatment does not substitute the requirements for landfills as a variety of residuals still need disposal.
- II. Permit the recovery of energy from the solid waste stream.
- III. Permit for minerals and chemicals recovery from the solid waste stream followed by reuse or recycling.
- IV. Remove a number of contaminants that the waste stream could content [17].

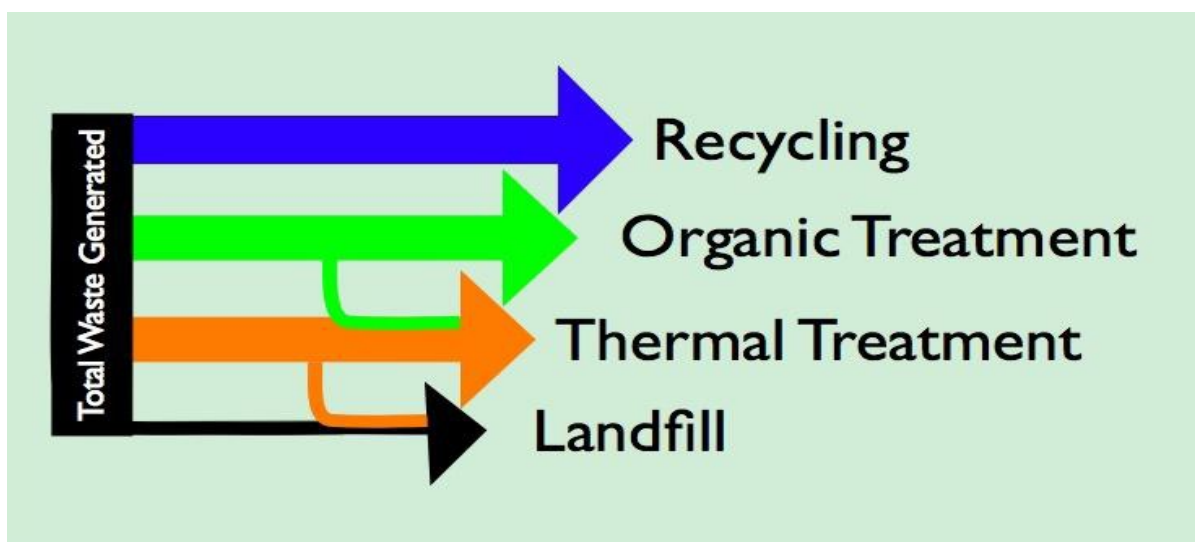
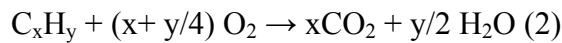
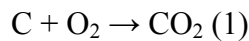


Figure 6. The Role of Thermal Treatment in Waste Management [17].

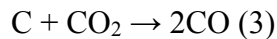
5.1 Combustion

Combustion is a process with full thermal degradation of a matter in an oxygen-rich environment which oxidizes the fuel completely. The characteristic of combustion of a waste stream is the excess air which is required for a complete oxidation and at temperatures higher than 850°C. The process produces a gas composed mainly of carbon dioxide (CO₂) and water (H₂O) and other emissions such as are nitrogen oxides, sulphur dioxide, etc. The inorganic part of the waste is converted to ash [15].

All the processes consist of converting the waste content into gas, liquid and solid products and at same time release thermal energy. Additional air emission is nitrogen oxides, sulphur dioxide, etc. The inorganic content of the waste is converted to ash. Incineration is the most common thermal process using a broad variety of fuels. During complete combustion oxygen is in excess and, as a result, the stoichiometric coefficient of oxygen in the combustion reaction is higher than 1. The reactions are as following:



If on the other hand oxygen is scarce, the reactions are described as incomplete combustion, and the produced CO₂ would react with C that has not been consumed.



The purpose of this treatment method is to decrease the volume of the treated waste and at the same time make use of the recovered energy which can be used as heating, steam production and electric energy production. The amount of net energy that can be generated per ton of domestic waste is typically about 0.7 MWh of electricity and 2 MWh of district heating.

This thermal treatment method could be practical for both the treatment of mixed solid waste and for the treatment of pre-selected waste. It can decrease the volume of the municipal solid waste by 90% and its weight by 75%.

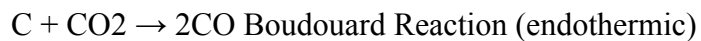
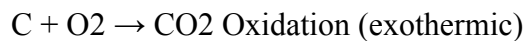
The incineration technology is however feasible for the thermal treatment of high amounts of solid waste usually more than 100000 tons per year [14]. Numerous conditions such as sufficient fuel material, achievable ignition temperature, suitable mixture proportion, continuous removal of produced gases and residues have to be fulfilled so that the full combustion of the treated solid waste can take place [14].

5.2 Gasification

Gasification is a thermal process that converts materials that contain carbon, such as biomass and municipal solid waste to syngas, which can subsequently be used to produce electric power and valuable products, like chemicals, fertilizers, steam and transportation fuels.

Gasification is partial thermal degradation of a substance without insufficient oxygen present for reaction of all hydrocarbons to CO₂ and H₂O. This incomplete oxidation process which produces syngas consist a mixture of varying amounts of hydrogen (H₂) and carbon monoxide (CO). The most important advantage of gasification of bio-waste is that the gas generated can be used directly, after cleaning, to fuel a gas turbine generator in a Combined cycle system, and therefore in theory improving the electrical efficiency of the plant. The major disadvantage is that would increase capital investment [14].

The key reactions during gasification are:



Existing gasification technologies normally utilize processed waste or RDF (Refuse Drive fuel) containing 6 to 7% moisture for syngas production. This moisture content permits hydrolysis and gasification to take place simultaneously. Temperatures normally used for gasification are between (600-1200)°C. Conversion efficiency can be different, but it can be up to 87% [18].

Gasification is different from incineration or combustion process, but a conversion process that generate more valuable and useful products from organic material even though both processes convert carbonaceous material to gases. Gasification processes operate in lack of oxygen or with insufficient amount of oxygen, whereas combustion processes operate with excess oxygen.

The combustion process is aiming to thermally destruct the feed material and to produce heat. In contrast, gasification aims to convert the material into more valuable, environmentally friendly products that can be utilized for a wide variety of purposes

From an environmental point of view, gasification waste offers a number one advantage over combustion of waste. First, emissions of sulphur and nitrogen oxides originator to acid rain, in addition to particulates from gasification are reduced considerably as a result of the cleanup of syngas. Sulphur in the gasifier feed is converted to H₂S, while nitrogen in the feed is converted to diatomic nitrogen (N₂) and NH₃. Both H₂S and NH₃ are removed later, generate a clean syngas. For this reason, if the clean syngas is combusted in a gas turbine for electricity production or in a boiler for steam generation or hot water, the production of sulphur and

nitrogen oxides are decreased radically. If the clean syngas is used as an intermediary product for chemical manufacturing, these acid-rain originators are not formed [14].

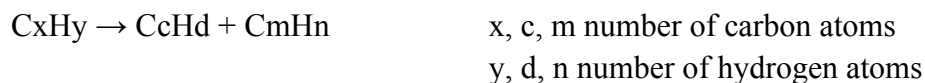
5.3 Pyrolysis

Pyrolysis refer to thermal degradation of substance by the use of an indirect, external source of heat, usually at temperatures between 450 to 750°C, complete absence of oxygen. Which drives out the volatile fraction of the organic materials. The product of this process is syngas composed mainly of H₂, CO, CO₂, CH₄ and long chain hydrocarbons etc. and has a net calorific value of between 10 and 20 MJ/Nm³.

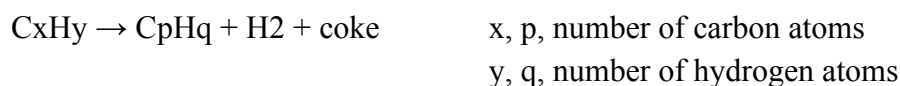
The syngas can be used in a verity of applications such as boilers, gas turbines or internal combustion engines to produce electricity. The remaining of organic materials that is non volatile is left as char material. The inorganic portion of the materials forms bottom ash that need to be disposed, even though some pyrolysis ash can be utilized for manufacturing brick materials. Pyrolysis causes thermal degradation of organic waste in oxygen deficient environment to produce a carbonaceous char, oils and combustible gases.

Though pyrolysis is an old technology, the appliance of it to biomass and waste materials is a quite recent development. Even though all the products of pyrolysis might be useful, the most important fuel for power generation is the pyrolysis oil, which can be used after further processing as liquid fuel in a boiler or as a replacement for diesel fuel in engines, depending on the process.

The reactions primarily are decomposition, where organic components of low volatility are transformed into more volatile ones:



Furthermore, in early stages of the pyrolysis process, condensation, hydrogen removal and ring formation reactions occur that initiate the formation of solid residue from organic material of low volatility:



However, if oxygen is present, CO and CO₂ are produced or there will potentially be some interactions with water. The products of pyrolysis can be liquid, solid and gaseous. The most part of the organic compounds in the waste are put through pyrolysis about (75–90) % are volatile substances and by (10–25) % form solid residue or so called coke. Because of the humidity and the existence of inorganic substances, however, the amount of volatile substances can be different from 60 to 70% and the coke between 30-40 percent[14].

In order to attain successful operation of a pyrolysis facility, constant control is essential because of the complex processes throughout the method development. Besides, solid waste with no large variation in the composition such as use of source separated waste or mechanically separated that does not contain metals and glass, can be fed on continuously or batch-wise.

Additionally the proportion of the pyrolysis product is highly relying on the waste composition and nature, the temperature conditions and the time of treatment.

Comparing to incineration the pyrolysis process has lower temperature, occur in reducing atmosphere and not in oxidizing. There is also higher ash content of carbon in contrast to incineration and the metal content in the waste are not oxidized during pyrolysis which increases its commercial value. Another advantage of pyrolysis is that it doesn't generate any ash when the pyrolysis gas is combusted and the off-gas is easier to clean. Furthermore the original volume of the waste comparing to incineration is decreased in higher level. However it should be mentioned that the major challenges with this technology today are product of pyrolysis cannot be disposed without any pretreatment is that waste pre-treatments like cutting and separation is necessary before pyrolysis which increase the operation costs and the large scale applications are limited [14].

6. Objective

The objective of this work was to investigate whether a thermal pretreatment of municipal solid waste could increase the stability of the material and consequently lead to better transportation opportunities and at same time reduce the amount of work needed for handling of municipal solid waste though thermal pretreatment.

7. Materials and method

A literature study was conducted to compile information about waste, science equipment, sampling for experiments, treatment of waste fuel and ancillary data and previous studies. Knowledge compilation is based on existing technical reports, technical specifications and manuals for science equipment, and how sampling should be performed on solid materials.

7.1 Origin and the characteristics of the material

The material is from a big municipal solid waste container located in Borås, Sweden in 2008. In the first step a fictitious reference sample of this container was taken and mixed properly. This sample had a quantity of 4 tones and represents the composition of the container. Measurements were done and it was estimated that both samples had a low Standard deviation, which showed that the two samples were similar in terms of net calorific value. From these tests, the sample is said to be a good reflection of container content. In the next step (2) a second sample was taken from mixture in the step (1) and mixed well. This sample was about 50 kg. In step (3), after mixing two more samples were taken from sample in step (2). One with a quantity of 25 kg and the other 12.5 kg and so on. All the samples were analyzed to determine the size of the source of the error and from the results it was estimated

that the all the samples could be representative of the container. The material used in this project comes from step 3, sample (b) according to Figure 7. The composition of this sample was characterized by BELAB AB (Bränsle och Energilaboratoriet AB) in Norrköping, Sweden according to standard methods and the results are summarized in Appendix 1 and Appendix 2. The samples were further thermal pretreated in the lab at different temperatures.

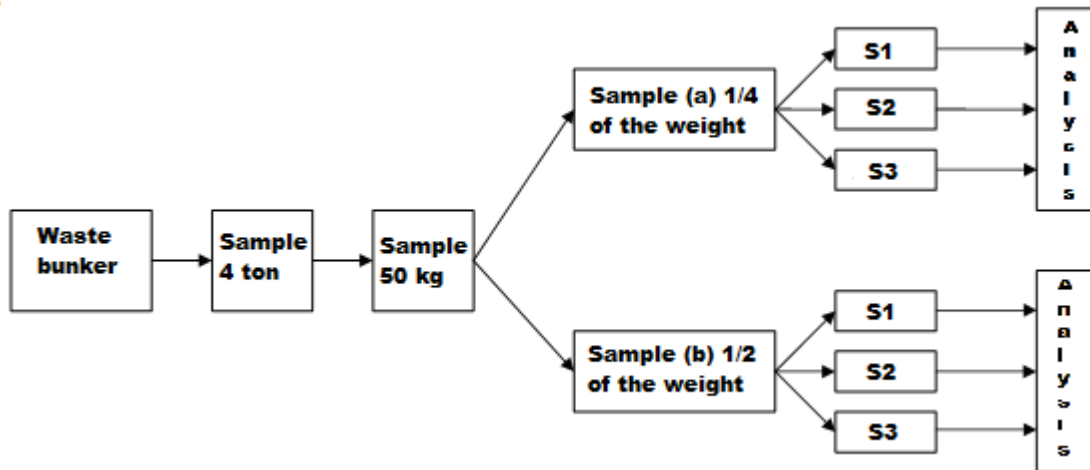


Figure 7. Estimated the samples

7.2 Experimental background

In this study, pyrolysis characteristics apply to MSW and this has been investigated, using a thermogravimetric analyzer (TGA). Thermogravimetric analyzer from Rubotherm monitors changes in the sample at very high temperatures and pressure. Benefit to the instrument performance is its magnetic coupling and control system that enables high-precision instrument which is in a separate chamber. This design allows for continuous tests can be considered over time while subjected to pressure and temperature variations and provide more accurate and safer measurements.

Some zero measurements were performed on the newly installed TGA in order to improve understanding of the data provided in the form of registered measuring temperature (T), pressure (P) and mass reduction (m).



Figure 8. Roubuterm thermogravimetric (TG)

7.2.1 Analysis procedure

Thermal gravimetric analysis (TGA) is a thermal analysis technique used either to decide alteration in sample weight as a function of temperature or as a function of time at constant temperature.

TGA was used to study the thermal treatment of samples in the experiment. Experiments were carried out on TGA at a steady level of heating or so-called T-ramp at $5^{\circ}\text{C}/\text{min}$ within a temperature range from $(20-750)^{\circ}\text{C}$ with a steady gas flow rates $100\text{ ml}/\text{min}$ (sample 8 to sample 12). The reason for choosing this temperature range $(20-750)^{\circ}\text{C}$ is to measure the mass loss rate of the material as function of time and also the lower temperatures in the experiment cause larger portion of the material is left after the experiment. Sample mass approximately 500 mg of fine fractional waste mixture used for the experiment and the enforcement of degradation to smaller fractions and the release of amounts of volatile substances, which are used to study the kinetics. Pyrolysis experiments were conducted in a device of pre-heating, pyrolysis and a condenser part (Figure 8).

The sample was confined in a small beaker (figure 9) placed in a reactor tube placed into the reactor section. The tube dimensions for the outer diameter (20 mm), wall thickness (2 mm) and length (250 mm). The temperature of the radiation source was measured with three thermocouples in the surface of the tube. Gas temperature in the reactor was measured by a thermocouple in the quartz tube from above. The device contains six thermocouple. The used gases had a purity of 99.9% . The gas acts as a carrier gas in the experiments to ensure that "pyrolysis" takes room in an inert atmosphere.

The valves were adjusted to shut off automatically and open up when the predefined temperature is reached. Carrier gas used in this experiment was N_2 or CO_2 to ensure an O_2 -free pyrolysis. In the first attempt the weight of the sample was 100 mg and the gas flow was about $50\text{ ml}/\text{min}$. All samples were heated in the interval of $(25-500)^{\circ}\text{C}$ at $5^{\circ}\text{C}/\text{min}$. Carrier gas was then switched to a mixture of 67% N_2 and 33% CO_2 , and temperature ranges were changed to $(100-450)^{\circ}\text{C}$ at $5^{\circ}\text{C}/\text{min}$ to see how the materials reacts with different temperature. The condenser contained water medium, which reduced the temperature of the

volatile compounds to below 100°C. Product formed is in the form of powdered black residue (Figure 10) and condensed gas.



Figure 9. Powdered black residue before treatment



Figure 11. Powdered black residue after Treatment

To control if there is biological activity in the samples thermally pretreated and untreated waste samples were incubated on an agar plate at 30°C for 14 days. After that the samples

were incubated additionally for 180 days at atmospheric temperature. Samples were incubated with four different conditions, with and without water, with water and nutrient addition, with water nutrient and M-Indicus addition. All samples were incubated in duplicates (figure 11).

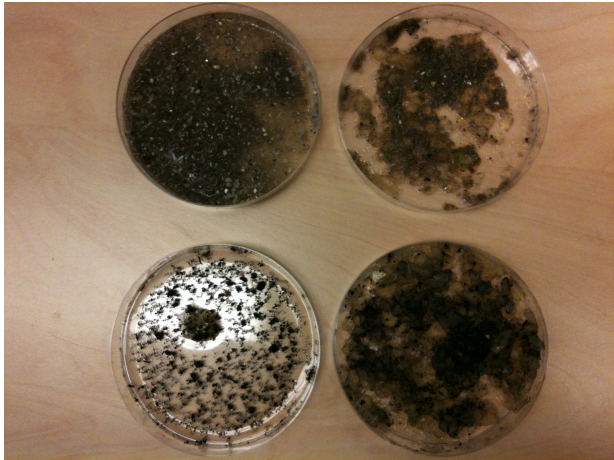


Figure11. Biological activity

8. Kinetic calculation

The kinetic expression for the overall reaction rate in gas–solid reactions is expressed according to (Feromos et al 2010)

$$(1) \quad dX/dT = k(P_g, T)f(X)$$

Where k is the reaction rate, in which the effect of temperature (T) as well as the partial pressure (P_g) of the gasifying agent is taken into account. The $f(X)$ expresses the alterations in the physical/chemical properties of the sample during gasification. The conversion ratio of the material/feedstock (X), and $f(X)$ are defined by following equations [19].

$$(2) \quad X = \frac{m_o - m_t}{m_o - m_\infty}$$

$$f(X) = (1 - X)^n \quad (3)$$

Where m is the initial weight of the sample and m_t is the weight of the sample at time t , and m_∞ the final weight of the sample in the reaction. In the second reaction n is the reaction order which is often in pyrolysis of biomass n is assumed to be a first-order reaction.

With assumption that the partial pressure of the gasifying agent is constant throughout the process, the temperature dependent reaction rate can be expressed by the Arrhenius equation, as the following:

$$k = k_0 e^{\left(-\frac{E}{RT}\right)} \quad (4)$$

Where k_0 is the pre-exponential factor, E is activation energy, R the universal gas constant (8.314 J/k_mol), and T is temperature. Assuming unity for the order of reaction ($n = 1$) the following equation can be represented by the [20]:

$$dX/dT = k (1 - X)^n$$

The logarithmic form is eq. (4) written: (5)

$$\ln k = \ln k_0 - E/RT \quad (6)$$

And the integration of eq. (4) is according to the following:

$$\ln\left(\frac{1-X_0}{1-X}\right) = K(t-t_0) \quad (7)$$

X_0 is the conversion of the sample at the start of gasification where $t=t_0$.

In order to calculate the kinetic parameters of the isothermal gasification of MSW samples, eq. (7)

was used. The $\ln(1-X)^{-1}$ was plotted versus gasification time ($t-t_0$) and thereby for a given material at various gasification temperatures, a set of data of rate constant can be obtained which this gives a straight line with the slope equal to the rate constant k . The kinetic parameters can be attained accordingly [20].

9. Resultat

9.1 Thermal decomposition of MSW

The MSW samples was investigate in TGA with seven different conditions at three different heating rates 5, 10 and 15°C/min with nitrogen and carbon dioxide gas. Each condition was repeated twice and the results are reported as an average. Data collected from this investigation is illustrated in Table 1. The experiment for sample 1 showed a weight loss of around 55% in a temperature range of (300-900)°C with N₂ and CO₂ gas and a gas flow of 50 ml/min at 1 bar and a heating rate of 10°C/min. Sample 2 was treated at the temperature range of (300-600)°C with a heating rate of 15°C/min, which resulted in a weight loss of approximately 47%. Sample 3 and sample 4 was treated at the temperature range of (20-400) °C with heating rate of 5°C/min and CO₂ gas with a flow of 100 ml/min. The treatment of sample 3 was carried out at a pressure of 10 bar and a resident time of 60 min and sample 4 at 1 bar and 90 min which resulted in weight loss of about 68% and 67% for sample 3 and 4 respectively. Sample 5, 6 and 7 were treated N₂ and CO₂ gas at 1 bar with a flow of 50 ml/min and a heating rate of 5 °C/min except with lower temperature range and resident time. When the temperature ranges were between (20-350)°C, with a resident time of 90 min, sample 5 showed a weight loss of 5%. Further decrease in temperature (160-250)°C and decrease of resident time to 60 min for sample 6 the weight loss were about 2.68%. Sample 7 showed a weight loss of 7.57% when it was treated in a temperature range of (120-350)°C with a resident time of 60 min. The figure 12, 13 and 14 which shows the curves of weight, loss versus temperature is noticeable that the most significant weight loss takes place in the initial step of the treatment.

After the thermal treatment, the treated materials (sample 6, sample 7 and sample 8) and the original sample was analyzed further and the results are summarized in Table 3. The moisture content is decreased considerably from 39.7% to 2.6% and 2.8% for sample 7 and sample 6 respectively after the treatment and the ash content were increased from 15.9 to 30.2% for sample 7 and 38% on a dry weight basis for sample 5. There was an increase of carbon content after the treatment from 27.8 % to 47.8 % for sample 7 and to 45.3 % for sample 5 and a slight decrease in hydrogen content from 8.1 to 5.7 and 4.4% for sample 7 and sample 5 respectively. The treatment increased the effective heating value at constant pressure by 3.04 MWh/ton for sample 1 and by 2.22 MWh/tonne for sample 5.

The weight loss conversion of the sample as a function of temperature at three different stages can be observed between the temperature intervals of (20-750)°C (Figure13). When CO₂ is used as gas, the first peak appears at 140°C which is loss of moisture content in the sample (approx10%). The second peak is at 270°C and around 60% of the weight loss occurs. The

third peak is at 360°C and the total weight loss is 96% and the remaining weight loss occurs after 360°C.

When the N₂/CO₂ gas is used (figure 14) the first peak is at 160°C and loss of moisture content in the sample is around 11%. The second peak appears at 360°C and around 69% of the weight loss occurs and the third peak is at 640°C and the total weight loss is 71%.

Using N₂ as gas the weight loss at the first peak at 150°C is approximately 8.3% and the second peak is at 360°C and around 71% of the weight loss occurs. The third peak is at 560 °C and the total weight loss is 87%.

Table1. Data from themogravimetric analysis of MSW with N₂/CO₂

Sample	Time (min)	Temp (°C)	T-ramp (°C/min)	Gas	Gas flow (ml/min)	Pressur (bar)	Weight % left
1	60	300-900	10	N ₂ +CO ₂	50+50	1	44.44
2	60	300-600	15	N ₂ +CO ₂	50+50	1	52.57
3	60	20-400	5	CO ₂ +N ₂	100+100	10	31.51
4	90	20-400	5	CO ₂	100	1	35.8
5	90	20-350	5	N ₂ +CO ₂	50+50	1	94.63
6	30	160-250	5	N ₂ +CO ₂	50+50	1	97.32
7	60	120-350	5	N ₂ +CO ₂	50+50	1	92.42
8	180	20-750	5	CO ₂ +N ₂ +O ₂	50+50+50	1	9.69
9	180	20-750	5	CO ₂ +N ₂	50+50	1	15.59
10	180	20-750	5	CO ₂ +O ₂	50+50	1	20.56
11	180	20-750	5	CO ₂	50	1	4.35
12	180	20-750	5	N ₂	50	1	28.74

Results from biological activity test showed that biological activity does exist for the untreated waste samples that contained water, nutrient, and M.Indicus after 14 days of incubation. However no biological activity could be observed in the thermal pretreated samples and the untreated sample without water, nutrient and M.Indicus. After 180 days of incubation in atmospheric temperature on the other hand, biological activity could be observed in untreated samples without any nutrient or water addition while no activity could be observed in the pretreated samples either with or without M.Indicus.

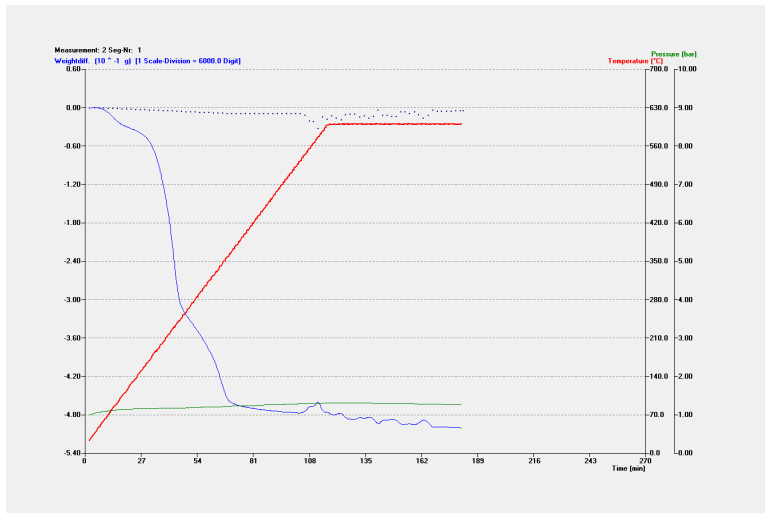


Figure 12. Weight loss vs. temperature in dynamic TG (heating rate, $5^{\circ}\text{C min}^{-1}$, CO_2)

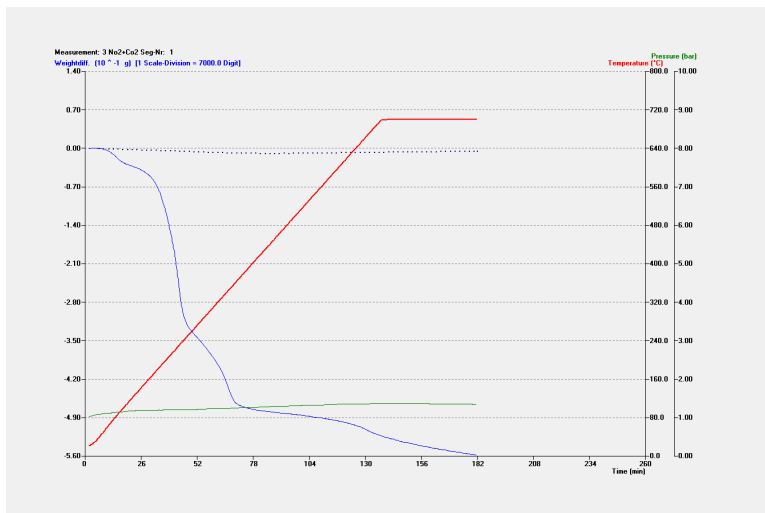


Figure 13. Weight loss vs. temperature in dynamic TG (heating rate, $5^{\circ}\text{C min}^{-1}$, N_2/CO_2 , gas flow 50ml/min, temperature interval $20^{\circ}\text{C}-750^{\circ}\text{C}$)

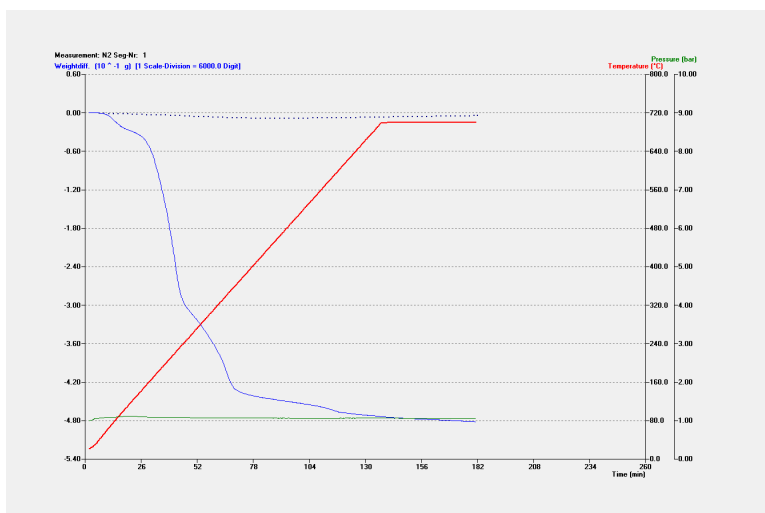


Figure 14. Weight loss vs. temperature in dynamic TG (heating rate, $5^{\circ}\text{C min}^{-1}$, N_2 gas flow 50ml/min, temperature interval $(20-750)^{\circ}\text{C}$)

Table 2. The activation energy (Ea) for decomposition reaction of MSW at different heating rate

Sample	Gas	A(S ⁻¹)	Ea(kJ/mol)
8	CO ₂ +N ₂ +O ₂	0.001	44.001
9	CO ₂ +N ₂	0.273	30.748
10	CO ₂ +O ₂	2.959	29.657
11	CO ₂	4.919	56.500
12	N ₂	0.001	15.063

Table 3. The content of ash, carbon, oxygen, hydrogen, sulfur, chloride, nitrogen and the calorific value of the MSW before and after thermal treatment.

Sample ¹	Moisture	Ash	C	O	H	S	Cl	N	Kal. (hv) (MWh/ton)
Original sample	39.7	15.9	27.6	47.1	8.1	0.1	0.37	0.8	3.187
5	0	15.9	46.1	29.9	6.0	0.16	0.62	1.3	5.285
6	2.6	30.2	47.8	14.3	5.7	0.362	0.56	1.08	6.101
7	2.8	38	45.3	10.6	4.4	0.303	0.37	1.02	5.212

¹Original sample is untreated, sample 5 is the dried original sample, sample 6 and sample 7 are treated samples

Discussion

Usually the products from the pyrolysis of MSW consist of a solid carbon-rich residue (charcoal) and a variety of volatile products. The extent and quality of the residue and the composition of the volatile fraction mainly depend on both the physical and chemical characteristics of the feed as well as on the process conditions. The chemistry of pyrolysis is not completely understood, and the heterogeneous nature of the MSW makes it even more difficult.

Activation energy (E_a) is defined as the minimum amount of energy required to initiate a chemical process. Kinetic study of the reaction shows that when the samples were run with only N_2 gas shows activation energy of 15 kJ/mol (Table 2), when CO_2 is added to the gas the activation energy increase to 30.748 kJ/mol. However, when only CO_2 is used, as gas the activation energy is 56.5 kJ/mol. When all the gases are used together ($CO_2+N_2+O_2$) it leads to increase of activation energy. It also can be seen that higher concentration of CO_2 in the process leads to increase the activation energy, which is not optimal for the reaction.

In another experiment the effect of CO_2 , N_2 and O_2 with different ratios on MSW was studied. The ramp selected was 10, 20 and $40^\circ C/min$. The results showed that the activation energy increased with the increase in O_2 concentration. It was also found that all the samples lost the majority the weight loss between $200^\circ C$ and $540^\circ C$, which is in accordance with this study, was around $300^\circ C$ and $500^\circ C$. Furthermore, the maximum weight loss rates showed also a increase with the increase in Oxygen concentration [21].

The rate of the kinetic process is dependent both on the temperature the sample is at, as well as the time it has spent at that temperature.

Another factor that has major effect on the untreated MSW is the moisture content in the material. The moisture content has a major effect on the material property and durability. MSW can have the ability to absorb high amount of water even though it is not in balance with the surrounding. This depends on how water is bound in the material structure. In order to release the moisture from the material structure energy is required in different quantities which is in turn dependent how the moisture is bound to the material structure. The treated material does not absorb any moisture.

Conclusions

From the study of thermogravimetric analysis of MSW composition, the following conclusions:

Pyrolysis is a technique that could be used as a method for pretreatments of waste.

The maximum rate of weight loss centralizes much of (300-500) °C. The weight losses of the absolute majority of samples are up to 95% at 750°C, which shows that the pyrolysis technique can remarkably reduce the mass of waste.

The maximum weight loss (40-70)% is between (200-450)°C. The remaining weight loss occurs above 450°C. In this temperature area (200-450) °C the oxygen concentration has apparent effect on the reaction rate. Comparing sample 8 and sample 9, it is obvious that the sample with oxygen has a weight loss of 90.3% which is higher than the sample without oxygen which was about 84.4%. Oxygen availability in the process affects the weight loss of the material and thereby the process resembles a combustion process and the MSW combustion produces CO₂.

It would be beneficial to maintain the material dry from moisture in order to produce maximum energy amount at incineration. However, this is not done today except when the material is stored during short period of time. The untreated sample in this experiment was containing 39% moisture content at 100% relative humidity and requires drying prior to incineration. A treated product will contain (2-3) % moisture at 100% relative humidity and requires no drying before incineration

Finally, from observations of biological activity test between treated and untreated samples it can be concluded that thermal pretreatment could be an alternative way for storage of waste for long period of time, which could have important impact in i.e. for transportation and durability during storage.

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Appendix 1

Analysis	Composition	Unit	Method/reference
Moisture content	39.7	%	CEN/TS 14774 / 14780
Ash content	15.9	% of TS	CEN/TS 14775 / 15403
Ash content Lev. State	9.6	%	CEN/TS 14775 / 15403
Sulphur S	0.16	% of TS	CENTS15289/15408/ASTM4239
Sulfur S Lev. State	0.10	%	CENTS15289/15408/ASTM4239
Chlorine Cl	0.62	% of TS	CENTS15289/15408/ASTM4208
Chlorine Cl Lev. State	0.37	%	CENTS15289/15408/ASTM4208
Carbon C	46.1	% of TS	CENTS15104/15407/ASTM5373
Carbon C, Lev. State	27.8	%	CENTS15104/15407/ASTM5373
Hydrogen H	6.0	% of TS	CENTS15104/15407/ASTM5373
Hydrogen H Lev. State	8.1	%	CENTS15104/15407/ASTM5373
Nitrogen N	1.3	% of TS	CENTS15104/15407/ASTM5373
Nitrogen N Lev. State	0.80	%	CENTS15104/15407/ASTM5373
Oxygen O (estimated)	29.9	% of TS	ASTM-D 5373
Oxygen O Lev.tillstånd (est.)	53.2	%	ASTM-D 5373
Silver Ag	0.32	mg/kg TS	NMKL161 mod.; ICP-MS
Aluminum Al	4100	mg/kg TS	NMKL161 mod.; ICP-AES
Arsenic As	92	mg/kg TS	NMKL161 mod.; ICP-MS
Barium Ba	120	mg/kg TS	NMKL161 mod.; ICP-AES
Boron B	7.6	mg/kg TS	NMKL161 mod.; ICP-MS
Calcium Ca	16800	mg/kg TS	NMKL161 mod.; ICP-AES
Cadmium Cd	0.45	mg/kg TS	NMKL161 mod.; ICP-MS
Cobalt Co	3.0	mg/kg TS	NMKL161 mod.; ICP-MS
Chromium Cr	140	mg/kg TS	NMKL161 mod.; ICP-AES
Copper Cu	220	mg/kg TS	NMKL161 mod.; ICP-AES
Iron Fe	3600	mg/kg TS	NMKL161 mod.; ICP-AES
Mercury Hg	68	mg/kg TS	NMKL170 mod.; AFS (kallf.)
Potassium K	3200	mg/kg TS	NMKL161 mod.; ICP-AES
Magnesium Mg	1600	mg/kg TS	NMKL161 mod.; ICP-AES
Manganese Mn	120	mg/kg TS	NMKL161 mod.; ICP-MS
Molybdenum Mo	2.3	mg/kg TS	NMKL161 mod.; ICP-MS
Sodium Na	5100	mg/kg TS	NMKL161 mod.; ICP-AES
Nickel Ni	8.1	mg/kg TS	NMKL161 mod.; ICP-MS
Lead Pb	18	mg/kg TS	ALC208:902; ICP-MS
Phosphorus P	1700	mg/kg TS	NMKL161.mod.; ICP-AES
Antimony Sb	1.4	mg/kg TS	NMKL161 mod.; ICP-MS
Selenium See	0.18	mg/kg TS	NMKL161 mod.; ICP-MS
Tin Sn	6.9	mg/kg TS	NMKL161 mod.; ICP-MS
Titan Ti	82	mg/kg TS	NMKL161 mod.; ICP-AES
Vanadium V	5.0	mg/kg TS	NMKL161 mod.; ICP-MS
Zinc Zn	360	mg/kg TS	NMKL161 mod.; ICP-AES
Silicon Si	32500	mg/kg TS	ALC208:201; AAS (flamma)

Appendix 2

Analysis	Before treatment	After treatment Sample 1	After treatment Sample 2	Unit
Moisture content, 105 °C	39.7	2.6	2.8	%
Ash content, 550 °C	15.9	31.0	39.1	% ds
Ash, 550 °C delivery	9.6	30.2	38.0	%
Carbon (C) delivery	27.8	47.8	45.3	%
Carbon (C) dry	46.1	49.1	46.6	% ds
Hydrogen (H) delivery	8.1	5.7	4.4	% *
Hydrogen (H) dry	6.0	5.5	4.2	% ds
Nitrogen (N) supply	1.3	1.08	1.02	%
Nitrogen (N) dry	0.80	1.11	1.05	% ds
Oxygen (O) supply	29.9	14.3	10.6	% *
Oxygen (O) dry	53.2	12.4	8.3	% ds
Chlorine (Cl) delivery	0.37	0.56	0.37	%
Chlorine (Cl) dry	0.62	0.58	0.39	% ds
Sulfur (S) supply	0.10	0.362	0.303	%
Sulfur (S) dry	0.16	0.372	0.311	% ds
cal. vv art. volume delivery	11.476	21.971	18.770	MJ/kg
Eff. vv art. pressure delivery	9.725	20.760	17.826	MJ/kg
Eff. vv art. pressure dry	17.734	21.379	18.410	MJ/kg
Eff. vv art. pressure dry ash-free	21.087	30.978	30.233	MJ/kg
cal. hv constant volume delivery	9.817	5247	4482	Kcal/kg
Eff. hv constant pressure delivery	2324	4957	4257	Kcal/kg
Eff. hv constant pressure dry	4238	5105	4396	Kcal/kg
Eff. hv constant pressure dry ash-free	5040	7397	7220	Kcal/kg
cal. hv constant volume delivery	4.942	6.101	5.212	MWh/ton
Eff. hv constant pressure delivery	2.726	5.765	4.950	MWh/ton
Eff. hv constant pressure dry	4.925	5.937	5.113	MWh/ton
Eff. hv constant pressure dry ash-free	5.856	8.602	8.396	MWh/ton

ds = dry sample, hv = heating value

Table 4 shows the final analysis of the material used in this work