

สำนักหอสมุดกลาง พระจอมเกล้าลาดกระบัง

**CORRELATION BETWEEN HEATING VALUE AND PROXIMATE
ANALYSIS OF SEWAGE SLUDGES**



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บทคัดย่อ

โครงการพิเศษนี้เป็นการศึกษาหาความสัมพันธ์ระหว่างค่าความร้อนกับการ
วิเคราะห์แบบประมาณของกากตะกอน โดยใช้วิธีดังต่อไปนี้ Proximate analysis Bomb
calorimeter และ Thermogravimetric Analysis โดยองค์ประกอบของกากตะกอนแสดง
ในหน่วยเปอร์เซ็นต์ต่อน้ำหนัก ค่าการให้ความร้อนและการสลายตัวโดยความร้อนของ
กากตะกอน และเปอร์เซ็นต์ของผลิตภัณฑ์ของกากตะกอน หลังจากนั้นนำค่าที่ได้จาก
Proximate analysis และ Bomb calorimetry มาวิเคราะห์หาความสัมพันธ์ของค่าการให้
ความร้อน กับองค์ประกอบของกากตะกอนแต่ละตัว โดยใช้ Regression Analysis

จากการศึกษาวิจัยพบว่า ตัวอย่างกากตะกอนจากโรงพยาบาลปทุมธานี มีค่าของ
ผลิตภัณฑ์ที่เป็นของระเหย มากถึง 53.25% รวมถึงมีค่าการให้ความร้อนสูงที่สุดถึง
2,571.36 Kcal/kg และเมื่อศึกษาความสัมพันธ์จาก Regression Analysis พบว่า
ความสัมพันธ์ระหว่าง ของระเหย คาร์บอนคงตัว และ เถ้าถ่านมีความสัมพันธ์กันดีที่สุด
เนื่องจากค่า the coefficient of determination มีค่าถึง 0.996

Special Project Title: Correlation between Heating Value and Proximate Analysis of Sewage Sludges

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ABSTRACT

This special project was studied the correlation between heating value and proximate analysis of sewage sludge by three following methods; proximate analysis, bomb calorimetry and thermogravimetric analysis. The composition of sewage sludge was shown in term of percent by weight, heating value and thermal decomposition of sewage sludge and percentage of sewage sludge's product. After proximate analysis and bomb calorimetry were analyzed, the heating value and sewage sludge composition were determined the correlation by using regression analysis.

From this research, it was found that the sewage sludge from Patunthani Hospital shown the most volatile matter to 53.25 wt% and specified the highest heating value to 2,571.36 Kcal/kg. The regression analysis indicated that the correlation between volatile matter, fixed carbon and ash had the best relationship.

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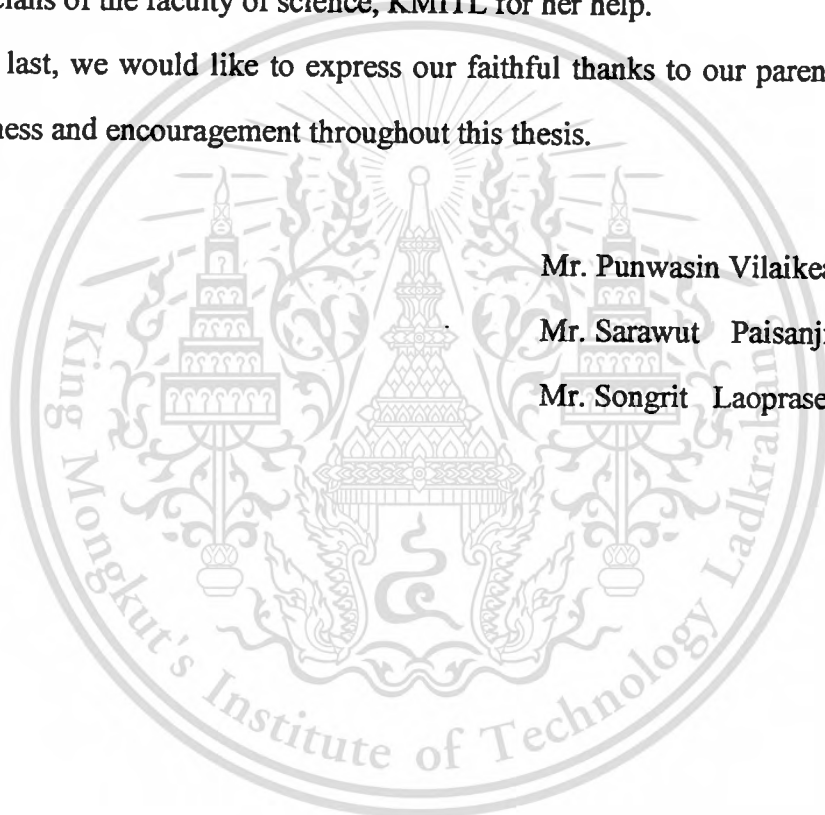


TABLE OF CONTENTS

| | Page |
|---|------|
| THAI ABSTRACT | I |
| ENGLISH ABSTRACT | II |
| ACKNOWLEDGEMENT | III |
| TABLE OF CONTENT | IV |
| LIST OF TABLES | VI |
| LIST OF FIGURES | VIII |
| CHAPTER 1 INTRODUCTION | |
| 1.1 Motivation | 1 |
| 1.2 Objectives | 1 |
| 1.3 Scope of study | 2 |
| 1.4 Expected results | 2 |
| CHAPTER 2 LITERATURE REVIEW AND THEORY | |
| 2.1 Literature review | 3 |
| 2.2 Related theory | 8 |
| 2.3 Typical pyrolysis process | 32 |
| 2.4 Pyrolysis and gasification of sewage sludge | 33 |
| 2.5 Pyrolysis and oil from sludge processes | 35 |
| CHAPTER 3 EXPERIMENTAL DETAILS | |
| 3.1 The chemicals used in the experiment. | 38 |
| 3.2 Instruments | 39 |
| 3.3 Flow chart | 40 |
| 3.4 Sewage sludge composition analysis | 41 |
| 3.5 Characterization of sewage sludge | 41 |

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TABLE OF CONTENTS (CONTINUED)

| | Page |
|--|------|
| CHAPTER 4 RESULTS AND DISCUSSION | |
| 4.1 Results from proximate analysis | 47 |
| 4.2 Results from bomb calorimetry | 48 |
| 4.3 Regression analysis | 48 |
| 4.4 Thermogravimetric Analysis (TGA) | 55 |
| CHAPTER 5 CONCLUSION AND RECOMMENDATION | 64 |
| REFERENCE | 66 |
| APPENDICES | |
| APPENDIX A | 69 |
| APPENDIX B | 71 |
| APPENDIX C | 77 |

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LIST OF TABLES

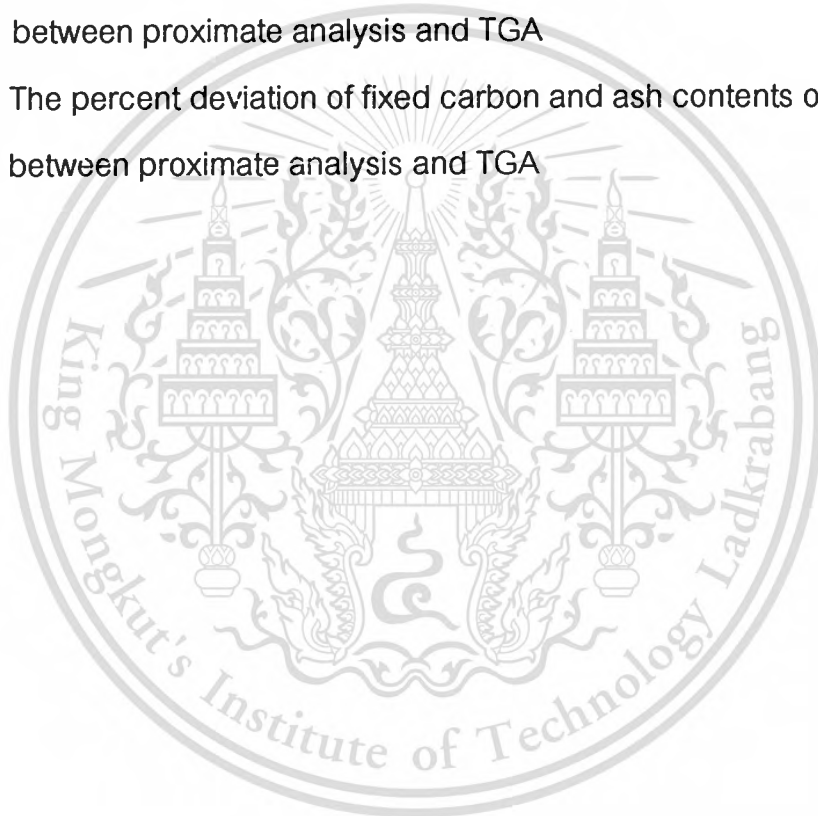
| | Page |
|--|------|
| Table 2.1 Comparison of national standards for effluents in mg/l | 9 |
| Table 2.2 Content of fertilizing compounds in municipal sewage sludge | 21 |
| Table 2.3 Contents of heavy metals in German sludges and soils | 22 |
| Table 2.4 Limit values of heavy metals stipulated in sludge in Agriculture Directive | 23 |
| Table 2.5 Some limit values of heavy metals stipulated in sludge from difference countries The limits are given in mg of metal per kg of sludge-dry mass basis | 24 |
| Table 2.6. Cost development of disposing sewage sludge with 35% dry mass | 26 |
| Table 2.7. The percent sewage sludge recycled and disposed of by the EU | 29 |
| Table 2.8 Comparison of oil yields (kg/kg daf sludge) from various groups | 37 |
| Table 3.1 List of source of samples | 38 |
| Table 3.2 Lists of instrument | 39 |
| Table 3.3 The analysis method of the sewage sludge composition | 41 |
| Table 3.4 Appropriate processing conditions of Thermogravimetric Analysis Method | 46 |
| Table 4.1 Proximate analysis of sewage sludge studied | 47 |
| Table 4.2 Heating values of sludge sample by bomb calorimetric method | 48 |
| Table 4.3 Summary six regression model and coefficient of determination (R^2) | 54 |

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Forbidden to modify the content, and cite the document when use.

LIST OF TABLES (CONTINUED)

| | Page |
|---|------|
| Table 4.4 Summary of sludge samples from TGA | 60 |
| Table 4.5 The percent deviation of moisture contents obtained between proximate analysis and TGA | 61 |
| Table 4.6 The percent deviation of volatile matters obtained between proximate analysis and TGA | 62 |
| Table 4.7 The percent deviation of fixed carbon and ash contents obtained between proximate analysis and TGA | 62 |



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LIST OF FIGURES

| | Page |
|---|------|
| Figure. 2.1 Material balance: water–solid mass according to Manzel | 14 |
| Figure. 2.2 A flow diagram of wastewater treatment plant at Koehlbrandhoeft-Hamburg, Germany | 16 |
| Figure. 2.3 Sludge production in Germany | 17 |
| Figure.2.4 Sludge production in the EC, 1984–2005 in million t/a dry sludge | 19 |
| Figure. 2.5 Sludge disposal routes in the European Community up to 2005 | 30 |
| Figure 4.1 Linear Regression of Heating Value vs. Volatile matter | 49 |
| Figure 4.2 Linear Regression of Heating Value vs. Ash | 50 |
| Figure 4.3 Linear Regression of Heating Value vs. Fix carbon | 51 |
| Figure 4.4 TGA thermograph of sludge sample 1 (9-12) | 55 |
| Figure 4.5 TGA thermograph of sludge sample 2 (8-11) | 56 |
| Figure 4.6 TGA thermograph of sludge sample 3 (8-10) | 57 |
| Figure 4.7 TGA thermograph of sludge sample 4 (m11) | 58 |
| Figure 4.8 TGA thermograph of sludge sample 5 (9-02) | 59 |

CHAPTER 1

INTRODUCTION

1.1 Motivation

Nowadays Thailand has been increased energy consumption for using in various types of industry as fuel, natural gas, electricity, etc. From this reason, the environmental problems have been come after energy uses. They cause reduction of resources and increment of pollution.

In this research we are interested in waste water pollution resulting from petroleum industry's waste products. The way to make it clean is purification processes. During the process, the residues have been occurred, calling sewage sludges. The disposing way of this waste products have been improved to development of civilization and technology. The sludge use mechanically dewatered process in order to reduce the amount of disposes. Even though the most primitive sludge treatment is on land or into seas, they are forbidden in many countries. Therefore the increasing amount of sludge, the more enhancing methods of sludge have to be developed. Those techniques are thermal sludge treatment and transform sewage sludge to be fuel as well.

1.2 Objectives

- 1.2.1 Added value of sewage sludge as fuel.
- 1.2.2 Study of sewage sludge decomposition by thermal process.
- 1.2.3 To determine calorific values of sewage sludge.
- 1.2.4 Investigation of sewage sludge by proximate analysis method.
- 1.2.5 Classification of sewage sludge composition.

1.3 Scope of study

- 1.3.1 Using thermogravimetric analysis for determining sewage sludge decomposition.
- 1.3.2 Using bomb calorimetry method for determine calorific value.
- 1.3.3 Analysis sewage sludge samples by proximate analysis method.
- 1.3.4 Classification of sewage sludge samples by using the data from thermogravimetric analysis method, the calorific value and proximate analysis method.
- 1.3.5 Determine the relation of volatile matter with the other properties of sewage sludge samples

1.4 Expected results

- 1.4.1 To understand the good correlation between crucial parameters of sewage sludge in different areas.
- 1.4.2 To identify the heating value of each area.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Literature Review

L. Shen and D.K. Zhang [1] studied on an experimental study of oil recovery from sewage sludge by low-temperature pyrolysis in a fluidised-bed. They found that a maximum oil yield of 30% (wt% daf basis of sludge fed) was achieved at a bed temperature of 525 °C and a gas residence time of 1.5 s. The oil yield reaches a maximum at 525 °C and decreases with increasing residence time. These trends are consistent with previous studies for sewage sludge. There is a clear evidence that secondary cracking reactions occur after 450 °C and for longer gas residence times. Also, the selectivity of the lighter oils increases at high temperatures as a consequence of cracking reactions.

M. Inguanzo, A. Domínguez, J. A. Menéndez, C. G. Blanco and J. J. Pis [2] studied on the pyrolysis of sewage sludge influencing of pyrolysis conditions on solid, liquid and gas fractions. They found that, at low temperatures, as the heating rate increases, cracking reactions are favored, giving rise to a higher concentration of light compounds in the pyrolysis oils. At temperatures above 650 °C, the effect of the heating rate is not as noticeable because at these temperatures the decarbonylation of oxygenated hydrocarbons predominates over cracking reactions. For fuels use, the organic fraction of the liquid pyrolysis products has heating values that are comparable to some conventional fuels. The potential that these products have for use as fuel is, therefore, high.

J. A. Menéndez, M. Inguanzo and J. J. Pis [3] studied on Microwave-induced pyrolysis of sewage sludge. They found that wet sewage sludge can be rapidly and efficiently pyrolyzed if some of the carbonaceous residue, which acts as a microwave receptor, is mixed with the raw material. On the other hand, if just the wet sludge is subjected to microwave action, only drying of the sludge takes place. Compared with conventional heating, microwave heating saves considerable time and energy for a similar degree of drying or pyrolysis. The microwave treatment of sewage sludge makes it possible to achieve a volume reduction of more than 80%, obtaining a porous carbonaceous residue of basic nature and providing a source of fuel gases and liquids.

R. Font, A. Fullana, J. A. Conesa and F. Llavador [4] studied on analysis of the pyrolysis and combustion of different sewage sludges by thermo gravimetric method. They found that from considering the seven samples of sludges with different origin and extensively characterized, it can be concluded that thermal decomposition obtained in pyrolysis and combustion can be associated with the origin of the sample. For aerobically stabilized sludges, the combustion apparently takes place by a first pyrolytic decomposition to 450–500°C with formation of char and then the combustion of char takes place above 450–500°C. For non-aerobically stabilized sludges, the combustion can be considered as an oxidative pyrolysis without the extensive formation of char that is burnt at high temperatures. An analysis of the biochemical stabilization can be obtained from the comparison between the TG runs of pyrolysis and combustion, although more experimental results are required to confirm this hypothesis.

W. Beckers, D. Schuller and O. Vaizert[5] studied on thermolytical treatment of dried sewage sludge and other biogenic materials—including upgrading of pyrolysis vapours by a cracking catalyst and examination of heavy metals by X-ray fluorescence. They found that all three runs yield oil in equal proportion—roughly a quarter of the organic material is converted to oil. The oils are oxygenated and in the case of the sewage sludge contain nitrogen. In comparison with the corresponding feedstock, the oxygen content is reduced. The other product fractions vary. Lacquered wood has the highest proportion of gas (37%). Sewage sludge with the highest content of ash has the highest proportion of coke (27%). The run with sewage sludge yields the catalyst with the lowest content of coke deposited on the catalyst (3.2%). Linoleum contains barium (2.7%) which is released during pyrolysis and obviously is adsorbed on the surface of the catalyst. A high percentage of methane in the product gas is outstanding. In spite of high zinc concentrations (ca. 1%) in lacquered wood, the element zinc did not accumulate on the surface of the catalyst, although relatively large amounts of it left the reactor. If one follows the system library of the GC-MS, phenolic compounds should be in abundance alongside pure hydrocarbon aromatics. Results are not cited here. Compared with our results from earlier runs with sewage sludge, condensates have improved because of controlled addition of lime and the upgrading by the cracking catalyst. The accumulation of calcium and probably of potassium on the surface of the catalyst might be a problem, but it could be minimized by preparing appropriate particle diameters in the feedstock. The liquids from sewage sludge pyrolysis do not polymerize (viscosity does not visibly change in the course of 1 year). A shift has taken place to a more stable spectrum of organics. In the literature, large tar production is mentioned because organics

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are not upgraded. Oils resulting from condensers meet the specifications of analyzed liquids from other sources (i.e. bio oils) under the following aspects: organic elemental composition and traces of metals, heavy metals included. X-ray fluorescence has proved to be a good tool to evaluate heavy metal contents of feedstocks and product fractions. The concentrations of other elements are also detectable. Halogenation can be identified, especially in oil. Light elements like magnesium and phosphorus obviously cause a problem, although no reasonable explanation exists; this is probably an inherent disadvantage of the analytical method. A separation of pyrolysis and upgrading has proved to be successful insofar that it is technically feasible. No blocking of the sintered metal has been observed. Only traces of the processed material penetrated the catalyst. A long-term application of sintered metal has to be tested. An activity test for the missing catalyst is to evaluate the catalyst after use and regeneration. For further experiments, variation of technical parameters, e.g. vapours/catalyst ratio and temperature, are of crucial interest. A complete thermolytical treatment, which takes into account an ecological balance, must give perspectives for the future treatment of, up to this point, 'unusable' products. Coke and water from pyrolysis processes are problematic materials. In our case, this also applies for the liquids from the cyclone behind the catalytic reactor; it still has the consistency of a liquid. Clean gasification within the whole process of thermolytic treatment might offer a perspective for the detrimental substances.

M. Inguanzo, J. A. Menéndez, E. Fuente and J. J. Pis [6] studied on reactivity of pyrolyzed sewage sludge in air and CO₂. they found that the reactivity of the carbonaceous materials obtained from pyrolyzed sewage sludge depends on both the pyrolysis temperature and the heating rate at which the samples were obtained. In the case of reactivity with air the former effect is greater during the initial stages of the reaction. However, as the reaction progresses, the reactivity becomes more influenced by the heating rate than by the final pyrolysis temperature. The reactivity of the carbonaceous materials to CO₂ is considerably lower than reactivity to air, and proceeds in a more progressive way and there are no differences between reactions with structures of different reactivities. In this case, differences in reactivity are more affected by the heating rate than by the final pyrolysis temperature. Although the interpretation of the findings is not straightforward, the quantity of ashes (and in consequence the amount of reactive organic matter) and the higher densification undergone by the samples seem to account for the decrease in reactivity as the pyrolysis temperature and heating rate increase.

2.2 Related Theory

2.2.1 Sewage sludge: formation, treatment and disposal

2.2.1.1 Formation of sewage sludge

Sludge is formed during wastewater treatment. Wastewater is a combination of the liquid- or water-carried wastes removed from residential, institutional, commercial and industrial establishments, together with ground water, surface water and storm water, as may be present. Wastewater may contain certain undesirable components, including organic, inorganic and toxic substances, as well as pathogenic or disease-causing micro-organisms. The main groups of the organic solids in wastewater are proteins, carbohydrates, fats and oils. Protein contains about 16% nitrogen, and together with urea are the major sources of nitrogen in wastewater. In its untreated form, wastewater can not be disposed of for several reasons. First, the biological decomposition of the organic materials in wastewater consumes oxygen and thus reduces the quantity available in the receiving waters for the aquatic life. The decomposition also produces large quantities of malodorous gases. Secondly, the numerous pathogenic or disease-causing micro-organisms in untreated wastewater are health hazards to human beings. Third, its toxic compounds, especially heavy metals, can be dangerous to both plants and animals, and finally the presence of phosphates and nitrogen may lead to uncontrolled growth of aquatic plants. It is therefore necessary to reduce the organic components, nitrogen and phosphorous, toxic compounds, as well as to destroy the pathogenic or disease-causing micro-organisms from wastewater before its disposal.

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There are regulations governing the quality of the effluent discharged from Sewage Treatment Works (STW). The regulations set limits for the concentrations of BOD₅, COD, total suspended solids, phosphorous, nitrogen, mercury and phenol, among others, in the discharge from STW. In the European Union (EU), the quality of effluent is currently regulated through the Urban Wastewater Treatment Directive (91/271/EEC) of May 1991. The directive also requires that all communities with above 2000 population equivalents install adequate collection, treatment and disposal systems for the wastewater generated. Table 2.1 gives some values of the national standards of some countries for illustration.

Table 2.1 Comparison of national standards for effluents in mg/l [7]

| | Hong Kong | Japan | Malaysia | Singapore | Taiwan | France | NL | Portugal | EU |
|------------------|-----------|-------|------------|------------|--------|--------|-------|----------|-------|
| BOD ₅ | 20-40 | 160 | 20-50 | 100 | 100 | 30 | 20 | 40 | 25 |
| COD | 80-85 | | | | | 90 | | 150 | 125 |
| SS | 30-40 | | | | | 30 | 30 | 60 | 35 |
| N | 20-50 | | | | | 10 | 10-15 | 15 | 10-15 |
| Hg | 0.001 | 0.05 | 0.005-0.05 | 0.001-0.05 | 0.005 | | | | |
| Phenols | 0.1 | 5 | 0.001-1 | <5 | 5 | | | | |

It is important to note that even the Newly Industrialized Countries (NIC) are already moving towards stricter limits for pollutants in their effluent discharges. To achieve the set limits for effluent discharges, a modern wastewater treatment plant may employ three stages of wastewater treatment,

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i.e. mechanical, biological, and an additional (third) stage for the elimination of nitrogen and phosphorous.

The mechanical stage provides a primary clarification. The incoming untreated wastewater passes through racks and screens where coarse solids are removed, and then into grid chambers, where sand, gravel, cinders and other heavy solid materials are separated. Thereafter, in sedimentation tanks, readily settleable solids and floating materials are removed. In the mechanical stage, 50–70% of the suspended solids and 25–40% of the BOD_5 can be removed. The materials removed from primary sludge, having 3–5 wt% solids which consists of 30% inorganic and 70% organic matter.

In the biological treatment phase, the coagulation and removal of the non-settleable colloidal solids and the stabilization of the organic matter is accomplished biologically using a variety of micro-organisms, principally bacteria. The micro-organisms convert the colloidal and dissolved carbonaceous organic matter into various gases and cell tissues. The cell tissues have a specific gravity slightly higher than that of water and can therefore be removed through sedimentation. The sludge removed at this stage is normally referred to as secondary sludge.

In the third treatment stage, the elimination of phosphorous and nitrogen takes place. Nitrogen elimination may be achieved by a two-stage process: nitrification and denitrification. Ammonia in the wastewater is first oxidized to nitrate (nitrification) and thereafter the nitrate is converted to free nitrogen (denitrification) before it is discharged. Denitrification is an important part of the nitrogen cycle, since through the release of the nitrogen to the atmosphere, the cycle is completed. Phosphorous compounds can be eliminated through

chemical precipitation using additives followed by the sedimentation of the sludge formed, or through biological treatment, where phosphorous compounds are incorporated in the cell tissues which are thereafter removed through sedimentation. Nitrogen and phosphorous sludges may be formed at this stage

2.2.1.2 Processing of sewage sludge

Sludge is by far the largest in volume amongst the by-products of wastewater treatments, and its processing and disposal is perhaps one of the most complex environmental problems facing the engineer in this field. This is because the sludge resulting from the wastewater treatment operations and processes is usually in the form of a very dilute suspension, which typically contains from 0.25 to 12% solids, depending on the operation and process used. Apart from that, sludge is composed largely of the substances responsible for the offensive, pathogenic and toxic characteristics of the untreated wastewater. Sludge processing is therefore intended to reduce smell, reduce the quantity of the organic solids, eliminate disease-causing bacteria, improve the dewatering characteristics of sludge, and reduce the water content so that the end product can be treated further or disposed of with less handling problems and environmental consequences. These can be achieved through sludge stabilization, conditioning and dewatering.

A. Stabilization

There are three methods of stabilization normally practised in wastewater treatment plants. These are digestion, lime stabilization and heat treatment. Digestion involves partial conversion of the organic matter into a gas

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and a stabilized residue with the help of bacteria either in the absence of oxygen (anaerobic) or presence of oxygen (aerobic), during which disease-causing bacteria are also destroyed. Digestion is used widely for municipal sludge, but may not be applied to industrial sludge which may contain a high content of indigestible substances and/or chemicals likely to destroy the micro-organisms. Lime stabilization and conditioning involves the addition of lime to untreated sludge in sufficient quantity to raise the pH to 12 or higher, an environment that is not conducive to the survival of micro-organisms. Consequently, the sludge will not putrefy, create odours or pose a health hazard as long as the pH is maintained at this level. Heat treatment also stabilizes and conditions sludge. It involves two-stage heating of sludge, at 30–75 and 75–190°C, and at a pressure of 26 bar for a short time. This coagulates the solids, breaks down the gel structure and reduces the water affinity of the sludge solids. As a result, the sludge is sterilized, practically deodorized and is dewatered readily on vacuum filters or filter presses to 35–40% drymass without additives.

The methods of sludge stabilization and conditioning chosen are important since they determine the quantity of sludge to be further treated. They also change the physical and chemical characteristics of the sludge, and these may have significant effects on sludge incineration. Stabilization through digestion, e.g. leads to a decrease in the quantity of sludge, since part of the organic substance is released as CH_4 and CO_2 . This, however, reduces its calorific value from around 17.5 MJ/kg d.m. for raw sludge to about 10.5 MJ/kg d.m. for digested sludge, so it can be argued that incorporating digestion process would be undesirable if the sludge is to be incinerated. But, Albrink et al. have shown that digestion of sludge prior to incineration has several

advantages which outweigh the effect of reduced calorific value. The sludge volume is reduced by 50% and its dewatering properties increased by two–three points. Furthermore, in the event of a breakdown of the incinerator, digested sludge can be handled easier than raw sludge. The digestors could also provide short term storage of sludge. Lime stabilization leads to an increase in the quantity of sludge and lowers its calorific value. For sludge disposal through land filling, the addition of lime would increase the disposal cost. Thermal stabilization and conditioning cause insignificant changes in the quantity of sludge, but experience from large scale application shows that due to the return of the dissolved organic substance, heavy metals and NH_3 are returned back to the raw wastewater, the quality of effluent decreases. In the European Union, 50% of the sewage treatment plants have anaerobic digestion, 18% aerobic digestion and 4% lime stabilization, whereas 24% of the plants undertake no sludge stabilization. Digestion is therefore the most popular sludge stabilization method within the EU. Significant reduction in sludge quantity is achieved through digestion, which is in line with European Waste Management Policy of sustainable development having the following hierarchy of waste management priority: avoidance, minimization, recycling, incineration with energy recovery and landfilling.

B. Dewatering

The effect of moisture content on the sludge volume is enormous, and sludge handling techniques are directed toward reducing the moisture content and hence the volume of the sludge to be disposed. Dewatering is therefore a prerequisite for the further treatment of sludge, as well as handling, transporting and disposal. The moisture associated with flocs of sewage

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sludge are: 70–75% free water, 20–25% floc water, and 1% each capillary and bound water. The free water can be removed by thickening. The floc water is trapped in the interstices of floc particles and is separable only by mechanical dewatering. The capillary moisture can be removed mechanically only after chemical conditioning, whereas the bound moisture is separable only through cell destruction.

The water content of sludge after thickening, conditioning, mechanical dewatering and drying was shown in Fig2.1. Thickening leads to a significant volume reduction of the sludge. For example, thickening of sludge from 3 to 6% solids will reduce its volume by 50% . After thickening, further removal of water would require mechanical dewatering. To improve the dewatering properties, sludge may be conditioned using chemical additives or through thermal treatment. Chemical conditioning results in coagulation of the solids and the release of the water. The quantity of chemicals required is small (8–10 mg/kg d.m.) and therefore does not affect the quantity of sludge produced. Sludge incineration ash, fine sludge particles or coal can also be used as additives for sludge conditioning.

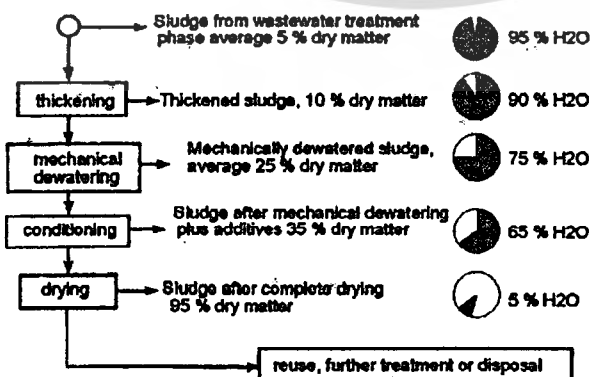


Fig. 2.1 Material balance: water–solid mass according to Manzel. [8]

The heat treatment process is applicable to biological sludge that may be difficult to stabilize or condition by other means. Mechanical dewatering units include belt filter press, vacuum filters and centrifuges. The solid contents achievable (with flocculants) range from 20 to 40 wt% for belt and centrifugal filters, and from 24 to 42 wt% for pressure and vacuum filters. Through thermal drying, a further reduction of the water content of the sludge can be achieved. Predried sludge is easier to store, transport and feed, and therefore offers wide possibilities for use. A pre-condition for the incorporation of the drying process is the presence of a clear disposal concept for the sludge. For example, sludge pyrolysis, gasification and co-firing in pulverized coal combustors may require complete dry sludge, whereas for mono-combustion, mechanically dewatered sludge with 20–45 wt% d.m. or semi-dried sludge with 45–60 wt% d.m. is used.

2.2.1.3 Production of sewage sludge

The world is currently witnessing a rapid increase in sludge production, and this is expected to continue up to the early part of the next century. In both developed and NICs, the increase in sludge production is driven by the increase in the percentage of households connected to central treatment plants, the increasingly tightening of pollution limits on the effluent discharges, as well as the availability of technologies capable of achieving higher efficiency of wastewater treatment. The effect of the increase in environmental awareness in general can also not be ignored. On the other hand, due to ever increasing transportation and disposal costs, every effort is being made to reduce the quantity of sludge for disposal by increasingly lowering the water content of the sludge. The net quantity of sludge available for disposal therefore depends on

the financial, environmental and technological limitations of a given city or country.

The history of the wastewater treatment plant of Hamburg City, Germany provides a good illustration of the above case. Currently, about 40,000,000 litres of wastewater per day is treated in their modern three-stage wastewater treatment plant (Fig.2.2) In the process, 4000 m³/day sewage sludge with 3 wt% dry matter is formed. The sludge is thickened to 5–8 wt% d.m. and stabilized through anaerobic digestion. On leaving the digestors, the sludge is conditioned by warming to about 55°C using waste steam from a drier and adding polyelectrolyte (6–7 g/kg d.m.). The sludge is then dewatered in centrifuges to about 23 wt% d.m. thereby reducing its volume by 80%. The dewatered sludge is then dried to a solid content of 55% dry mass.

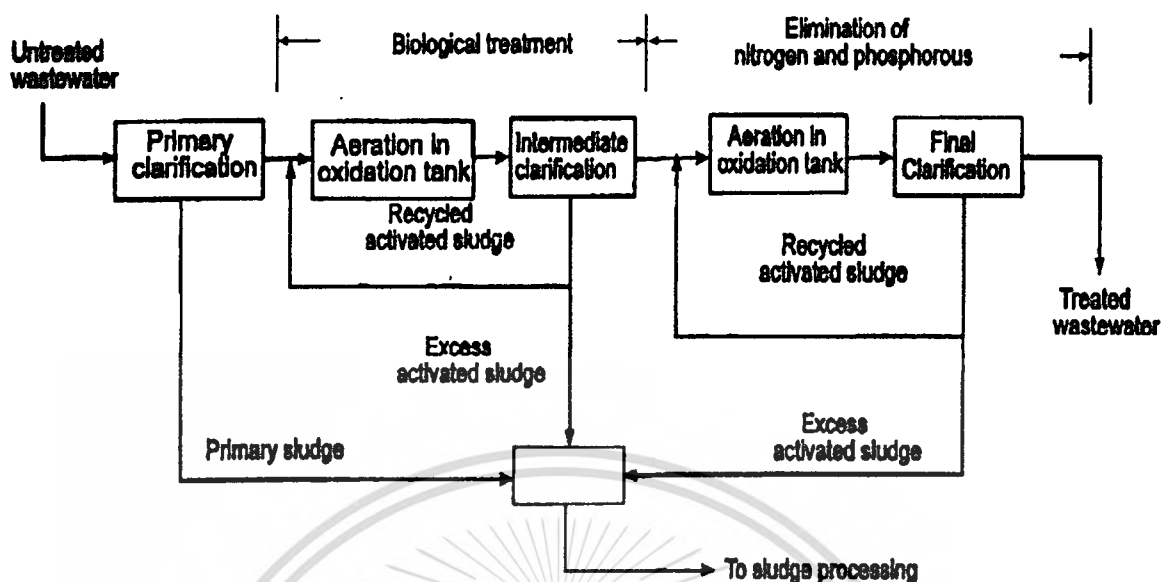


Fig. 2.2 A flow diagram of wastewater treatment plant at Koehlbrandhoeft-Hamburg, Germany [9]

The above described process has evolved over a long period. Up to 1981, the digested sludge was thickened and disposed of in the North Sea, and between 1981 and 1983, dumped in the Atlantic. The disposal of thickened sludge was uneconomical in terms of high transportation costs due to its large volume. Therefore, from 1983, the thickened sludge was conditioned with lime and then dewatered to 23 wt% d.m., and then raised to 35 wt% d.m. through additives for disposal in landfills. This resulted in a reduction of the quantity of sludge disposed from 300,000 tons/annum to under 100,000 t/a. However, following the commissioning of the second phase of the wastewater treatment plant in Koehlbrandhoeft in 1983 and the second biological treatment plant in Dradenau in 1988, the sludge quantity increased to 200,000 t/a. To reduce this, a drier was incorporated in the system in 1992 which raised the solid contents of the sludge to 55 wt% d.m. and reduced the quantity of sludge disposed to 70,000 t/a. Currently, a fluidized bed incinerator

is being commissioned to burn the 70,000 t/a sludge together with the 7,000 t/a screens and reduce them to 25,000 t/a stabilized ash.

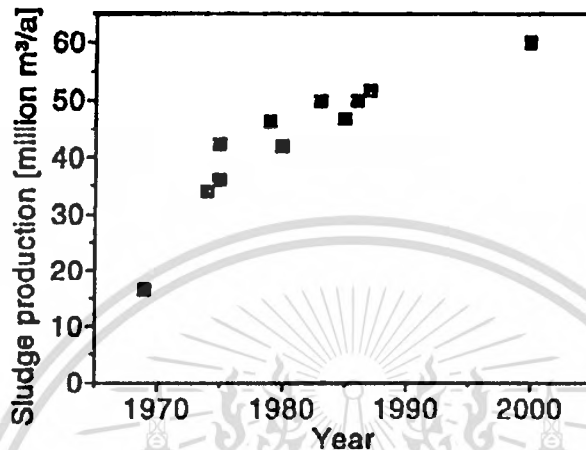


Fig. 2.3 Sludge production in Germany [10]

The above-described scenario from Hamburg's wastewater treatment plant represents a familiar problem of many cities of the developed countries in general, and Germany in particular. Around 10,000 wastewater treatment plants are currently operating in Germany. Some 2.5–3,000,000 tons of sewage sludge (d.m.) were produced in 1991, and by the year 2,000 about 4,000,000 tons per year is predicted. The expected increase in sludge production will be mainly due to increased connection of households in the former Democratic Republic of Germany, where only 56% of the households were connected to a central wastewater treatment system in 1994.

In the former West Germany, where already 90% of the households are connected to central treatment system, the expected increase will be due to improved quality and efficiency of wastewater treatment, especially with the addition of nitrogen and phosphorus elimination stages. Data compiled by Ying

show that there has been a steady increase in sludge production since 1965 (Fig. 2.3).

Outside Germany, the situation is more or less the same. In 1991, the countries within the European Union, having a domestic population of 345,000,000, operated 40,300 sewage treatment works yielding a total of about 6,500,000 tons of dry solids per year. This was an increase of 18% from the 5,500,000 tons of dry sludge produced in 1987. Currently, 79% of the populations are connected to sewer. Four countries (France, Germany, Italy and the UK) produce 84% of the sludge disposed of in the European Community and have 82% of the STWs. Germany alone contributes 41% of the total amount of sludge disposed compared with 17% from the UK, and 13% each from France and Italy. It is expected that sludge production will increase to about 10,000,000 million t/a d.m. by 2005 (Fig. 2. 4). The increase will be mainly caused by the implementation of the Urban Wastewater Treatment Directive (91/171/EEC), which requires all sewage discharges above 2,000 population equivalents to be treated according to the sensitivity of the receiving water, in specified phases, and to be completed by 31 December 2005.

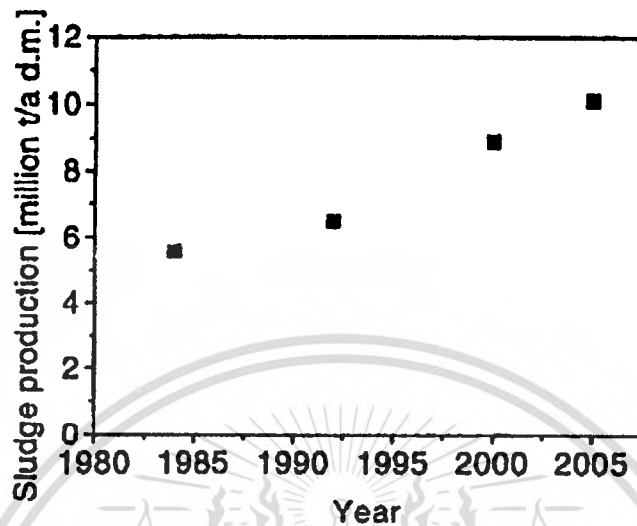


Fig.2.4 Sludge production in the EC, 1984–2005 in million t/a dry sludge.[11]

In the USA, over 7,000,000 tons of dry sewage sludge were produced in 1990 . The sludge disposed contained varying amounts of moisture contents so that the total mass actually involved might well have exceeded 70,000,000 tons per year.

In Japan, there has been a striking change in the provision of sanitary services during the last 30 years. In the early 1950s, almost all the population used a night soil collection system with relatively few sewage treatment plants being available. Since 1955, the urban areas have shown a rapid growth in the installation of flush toilets and sewer connection through a series of five-year programmes . Already in 1991, 45% of the households were connected to central sewage systems producing some 280,000,000 tons (about 4,560,000 t/a d.m.) of thickened sludge. Central government projected the sewer connection to increase to 54% in 1995 and 70% by the year 2000. Thus,

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a rapid increase in sludge production is expected in Japan. Reports by Lowe [12] indicate that in 1993, Hong Kong Territories, which include Hong Kong Island and the leased Territories on the South China mainland with an estimated population of 5,800,000 produced approximately 44,300 t/a dry sludge, of which 28,900 t/a were from water treatment and 15,400 t/a from sewage treatment .

The implementation of sewage treatment strategy and the need to satisfy the increasing demand for drinking water was expected to bring about a substantial increase in sludge production over the next decade. The expected increase in sludge production was due to the provision of new and improved treatment facilities, however, a significant increase was to be found after the commissioning of the Stonecutter Island STW. The Stonecutter plant alone was expected initially to produce 309,000 t/a dry matter of lime-precipitated primary sludge, rising to a peak of 314,000 t/a five years later. In other countries, the situation is expected to be more or less the same.

2.2.1.4. Disposal of sewage sludge

Generally, the selection of the best disposal route for the sludge from a particular treatment plant should start by identifying the most secure and environmentally acceptable final destination for the sludge, and this in turn would dictate the type of treatment required. This reverse sequence of selection procedures rarely occurs in practice and, indeed, sludge disposal has often been done on an ad hoc basis, with each sewage treatment plant management determining a local disposal solution. Currently, the sludge disposal outlets which exist are recycling as fertilizer, land filling, dumping in the sea and incineration.

A. Application of sewage sludge as fertilizers on agricultural land

Residues of treatment of municipal wastewater can be applied to the land to serve as a fertilizer and soil conditioner. Based on its content of nitrogen and phosphorus (Table 2.2), communal sludge shows good fertilizer properties. Sludge recycling as fertilizer has several advantages which include the return of the organic materials into the bio-cycle. Sludge also replaces the application of artificial fertilizers whose production also requires a lot of energy. Currently, application of sludge in agriculture takes 60% of the sludge produced in France, 54% in Denmark, 50% in Spain, 44% in UK and 26% in USA.

Table 2.2 Content of fertilizing compounds in municipal sewage sludge [13]

| Components | N | P ₂ O ₂ | K ₂ O | MgO | CaO |
|---------------------|-----|-------------------------------|------------------|-----|------|
| Average (kg/t d.m.) | 38 | 36 | 4.2 | 9.8 | 73.8 |
| Minimum (kg/t d.m.) | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 |
| Maximum (kg/t d.m.) | 246 | 344 | 95 | 122 | 727 |

In the recent past, the application of sludge on agricultural land has met a lot of setbacks due to the presence of heavy metals in the sludge. Analyses by Poletschny of 6,800 sludge samples from different parts of Germany have shown that the average content of heavy metals in municipal sludge is higher than the average for most farming soils (Table 2.3). This implies that

uncontrolled addition of sludge to the agricultural land may increase the concentration of heavy metals in the farm land. This could have an effect on the crop production due to uptake and also lead to the transfer of heavy metals to human beings through plants and animals.

Table 2.3 Contents of heavy metals in German sludges and soils [13]

| Heavy metal | Average in sewage sludge (mg/kg d.m.) | Average in farming soils (mg/kg d.m.) | Average in natural clays (mg/kg d.m.) |
|-------------|---|---|---|
| Cadmium | 3.8 | 0.44 | 0.3 |
| Copper | 330 | 15 | 45 |
| Nickel | 39 | 15 | -- |
| Lead | 159 | 36 | 20 |
| Zinc | 1318 | 67 | 95 |
| Mercury | 2.7 | 0.12 | 0.4 |
| Chromium | 91 | 25 | 90 |

To regulate the use of sewage sludge on agriculture, many countries have introduced limit concentrations either in the soil or sludge, and the frequency of application. For example, Table 2.4 shows the EU Directive governing the application of sludge to agricultural land.

Table 2.4 Limit values of heavy metals stipulated in sludge in Agriculture Directive [11]

| Heavy metal | Limit concentration in soil (mg/kg d.m.) | Limit concentration in sludge (mg/kg d.m.) | Limit annual average allowed in soil(kg per hectare per year) |
|-------------|---|---|---|
| Cadmium | 1-3 | 20-40 | 0.15 |
| Copper | 50-140 | 1000-1750 | 12 |
| Nickel | 30-75 | 300-400 | 3 |
| Lead | 50-300 | 750-1200 | 15 |
| Zinc | 150-300 | 2500-4000 | 30 |
| Mercury | 1-1.5 | 16-25 | 30 |
| Chromium | -- | -- | -- |

The Directive controls the use of sludge on agricultural land in two ways:

1. By considering the potential toxic elements (PTE) content of the soil nominated to receive sewage sludge. If the concentration of any one of the PTEs in the soil exceeds the minimum limit stipulated in the National Legislation used to implement the requirements of the Directive, then sludge application will not be allowed.
2. By regulating the application of sludge to land to ensure that the accumulation of heavy metals after sludge addition does not exceed the limits laid down in the legislation.

The EC directive is flexible in its approach to metal limits and this has led to most countries setting their own limits, some of which are more strict (see Table 2.5). In some cases, the nature of the soils also matters. For example, The Netherlands and Denmark have set very strict limits for metals in sludge applied to land due to the vulnerable shallow sand soils in these countries and also to the need for the land to take a large quantity of animal slurries.

Table 2.5 Some limit values of heavy metals stipulated in sludge from different countries. The limits are given in mg of metal per kg of sludge-dry mass basis [14]

| Heavy metal | EU | UK | Germany | Denmark | South Africa |
|-------------|---------|-----|---------|---------|--------------|
| Cadmium | 1-3 | 3 | 1.5 | 0.5 | 2 |
| Copper | 50-140 | 135 | 60 | 40 | 100 |
| Nickel | 30-75 | 75 | 50 | 15 | 15 |
| Lead | 50-300 | 300 | 100 | 40 | 56 |
| Zinc | 150-300 | 300 | 200 | 100 | 185 |
| Mercury | 1-1.5 | 1 | 1 | 0.5 | 0.5 |

B. Disposal of sewage sludge through land filling in sanitary sites

Disposal of sewage sludge to sanitary landfills still takes the bulk of sludges in developed countries. About 40% of the sludge produced in the European Union is disposed of through land filling. For Greece, Luxembourg and Italy, where 90, 88 and 85%, respectively, of the sludge is taken to landfills, it is the main sludge disposal method. In the U.S.A., 48% of the sludge produced in 1990 was deposited through land filling.

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There are two methods of land filling, i.e. co- and mono-disposal. Whereas co-disposal with other municipal waste is possible, in most cases mono-filling is practised. Although currently one of the main sludge disposal outlets, the future of sludge disposal through land filling is doubtful. One of the problems of land filling is the poor physical nature of the sludge resulting in handling and stability problems. It is desired that sludge for land filling should be well stabilized and dewatered to reduce the emission of odour, gas (e.g. CH₄) and percolating water. Because of the problems of stability, emissions of odour and gas, and pollution of the ground water, there is a trend towards establishing a minimum standard for the physical properties of the sludge for disposal in some countries in order to minimize these problems. For example, in Germany, currently sludge must have a minimum dry matter content of 35 wt% to be deposited in a landfill. This has the effect of increasing the total quantity of sludge to be disposed due to additives required to raise the solid content. Another problem is that the available capacities of landfill sites are diminishing and suitable regions where new filling sites could be constructed are limited. In certain countries, e.g. Germany, the procedure for obtaining permission to construct a new filling site is long and tedious. These problems have tended to increase the tipping charges, and the advantage of land filling as a cheaper disposal method than incineration is disappearing rapidly. Indeed, a comparative cost development compiled by Kassner is a good illustration of this (Table 2.6).

Table 2.6. Cost development of disposing sewage sludge with 35% dry mass
[15]

| Year | Land filling (DEM/t) | Dewatering, strengthening and land filling (DEM/t) | Dewatering, incineration and land filling (DEM/t) |
|------|-------------------------|--|--|
| 1980 | 5-15 | 20-50 | 100-150 |
| 1985 | 20-50 | 40-80 | 120-160 |
| 1990 | 50-150 | 90-170 | 150-230 |
| 1991 | 70-180 | 100-210 | 170-290 |
| 1992 | 100-450 | 130-480 | 200-500 |

To avoid the pollution on ground water due to decomposition of the organic matter in the sludge, a new governmental regulation, the Technische Anleitung Siedlungsabfall (i.e. technical guideline for handling and disposal of urban waste) of 1992 was released in Germany, which requires that from 2005, the organic content of any material to be deposited in the filling sites must be less than 5%. This obviously indicates that only incineration sludge ash will be landfilled. In the EC, the provisions on land filling are being finalized. The directive will stipulate minimum technical and administrative requirements for the operation of landfills. The co-disposal of the sludge with domestic waste will be allowed, but co-disposal with hazardous waste will be phased out within five years of adoption of the Directive .

C. Dumping of sewage sludge into the sea

In Europe, dumping of sludge into the sea is currently practised only by three countries, i.e. Ireland 35%, UK 30% and Spain 10%. Marine dispersal is controlled in accordance with certain requirements, e.g. the Oslo Convention for the protection of the North Sea and the North East Atlantic, and in accordance to licences issued under national legislation which take into account the quantity and quality of the sludge and the nature of the receiving area. In USA, ocean disposal by states having coastal line has been practised, but this was expected to be phased out because of changes in water pollution control regulation. In Europe, there will be no more dumping of sludge into the ocean as from 31 December 1998, when the North Sea Conference Agreement comes into force and sea disposal is banned.

D. Disposal of sewage sludge through incineration

The limitations facing landfilling and recycling, and the planned ban on sea disposal lead to the expectation that the role of incineration will increase in the future. Sludge incineration enjoys a combination of several advantages that are not found in other treatment alternatives, including a large reduction of sludge volume to a small stabilized ash, which accounts for only 10% of the volume of mechanically dewatered sludge, and thermal destruction of toxic organic constituents. Further, the calorific value of dry sludge corresponds to that of brown coal, and therefore through incineration this energy content may be recovered. In large urban areas where vast quantities of wastewater sludge is produced, lack of readily available disposal space and the need to minimize odor generation from landfillings and aesthetic objections of the nearby population makes incineration an attractive sludge disposal method. There

have been considerable improvements to the technology of incineration. Techniques are now available to control gaseous emissions and incineration costs are becoming much more competitive with other disposal options, to the extent that incineration is now seen as the only solution to the increasing problems of other sludge disposal options .

Already, incineration takes 24% of the sludge produced in Denmark, 20% in France, 15% in Belgium and 14% in Germany. In the USA and Japan, 25 and 55% of the sludge produced, respectively, is incinerated.

E. Current and future disposal routes for sewage sludge

The sludge disposal routes for all the countries within the EU in 1992 is summarized in Table 2.7. A total of 6,476,400 tons dry substance of sewage sludge was disposed, out of which 37% was recycled, 40% landfilled, 11% incinerated, 6% dumped into the sea and the rest disposed through other outlets. On average, equal quantities of sludge went to agriculture and landfilling, taking 37 and 40%, respectively, whereas the level of disposal through incineration and sea disposal was low. Preferences of individual countries are different. France, Denmark, Spain and UK dispose most of their sludge through recycling as fertilizer, whereas the rest use landfilling. Landfilling is the main disposal route for Greece and Luxembourg, and it is seen that UK, Ireland and Spain are the only member countries which will be affected when disposal to sea is banned with effect from 31 December 1998. Incineration is already widely practised in Belgium, Denmark, France and Germany.

Table 2.7. The percent sewage sludge recycled and disposed of by the EU[11]

| Country | Agriculture | Landfill | Incineration | sea | Other routes |
|-------------|-------------|----------|--------------|-----|--------------|
| Belgium | 29 | 55 | 15 | 0 | 1 |
| Denmark | 54 | 20 | 24 | 0 | 2 |
| France | 60 | 20 | 20 | 0 | 0 |
| Germany | 27 | 54 | 14 | 0 | 5 |
| Greece | 10 | 90 | 0 | 0 | 0 |
| Ireland | 12 | 45 | 0 | 35 | 8 |
| Italy | 33 | 55 | <1 | 0 | 11 |
| Luxembourg | 12 | 88 | 0 | 0 | 0 |
| Netherlands | 26 | 50 | 3 | 0 | 20 |
| Portugal | 30 | 60 | 0 | 0 | 10 |
| Spain | 50 | 35 | 5 | 10 | 0 |
| U.K. | 44 | 8 | 7 | 30 | 11 |
| Total | 37 | 40 | 11 | 6 | 6 |

The forecast of the trends in disposal routes up to 2005 is shown in Fig. 2.5. Despite the fact that landfilling is currently the most widely used disposal outlet, almost all the countries recognize that this outlet will not be sustainable at current or projected levels far into the future due to increasing competition for landfill space, higher cost, more stringent environmental standards and the implementation of policies to promote recycling. Some countries have introduced measures to promote the recycling of organic waste, and to limit methane and leachate emissions from landfill sites. Consequently, in the future in countries, e.g. Germany, Denmark and France, sludge will only be acceptable in landfills as incinerator ash.

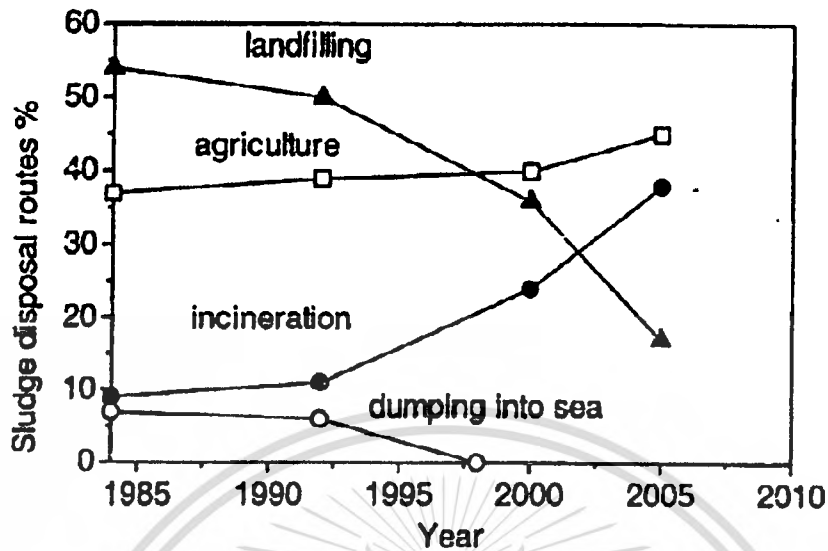


Fig. 2.5 Sludge disposal routes in the European Community up to 2005 [11]

As a result, landfilling as a way of sludge disposal is expected to decrease. On the other hand, many countries recognize agricultural land as the major beneficial outlet for sludge. Concern over risks from heavy metals and organic contaminants in the sludge, and caution over the addition of nitrogen- and phosphorous-rich manure to land, will continue to be a major factor in limiting the use of sludge as fertilizer. Incineration is currently a minor method of sludge disposal, but it is anticipated that it will increase substantially in the future to cope with the increasing sludge production from large STWs and to deal with sludge previously landfilled. In some countries, notably the Netherlands and to some extent Germany, sludge currently used as fertilizer will be incinerated, since agricultural use has become untenable in the Netherlands and regarded by many as increasingly difficult in Germany.

Projection shows that by 2005, recycling in agriculture will take 45% of the sludge produced in the EC. Incineration will increase to 38%, whereas only 17% of the sludge will be disposed through landfilling. The projections represent a very drastic reduction of the sludge to landfilling. The above-mentioned forecasts are strongly influenced by Germany, which will be producing up to 38% of sludge in the EC in 2005, and a strong decline in sludge disposal to landfill is mainly due to the anticipated implementation of the German policy to restrict the landfilling of organic matter-rich wastes by 2005 .

Although sufficient information is not available to us concerning the trend in other countries outside Europe, it may be expected that the role of incineration as a route for sludge disposal will increase. In Japan, e.g. over 55% of the sludge produced was incinerated in 1991 . The growing shortage of suitable land for disposal sites strengthens the preference for sludge incineration. Indeed, the pressure is so great that sludge incineration is already being seen as not good enough as far as volume reduction is concerned, and treatment techniques, e.g. sludge or ash smelting are currently being considered to give maximum volume reduction. In Hong Kong, there is no suitable agricultural land and forestry which can be utilized for sludge disposal. The disposal to sea is currently being practised for waterworks and digested sewage sludge. The Environmental Protection Department, however, is concerned about increasing the amount of sludge disposed to the relatively shallow marine site in the South China sea, and a comprehensive monitoring programme has been set up to assess its long-term effects. This, together with the international trend to ban sea disposal, led to the exclusion of the sea disposal option to all sludges other than those from Sha Tin

2.3 Typical Pyrolysis Process

Pyrolysis is formally defined as chemical decomposition induced in organic materials by heat in the absence of oxygen. In practice, it is not possible to achieve a completely oxygen-free atmosphere; actual pyrolytic systems are operated with less than stoichiometric quantities of oxygen. Because some oxygen will be presented in any pyrolytic system, nominal oxidation will occur. If volatile or semivolatile materials are present in the waste, thermal desorption will also occur.

Pyrolysis transforms hazardous organic materials into gaseous components, small quantities of liquid, and a solid residue (coke) containing fixed carbon and ash. Pyrolysis of organic materials produces combustible gases, including carbon monoxide, hydrogen and methane, and other hydrocarbons. If the off-gases are cooled, liquids condense producing an oil/tar residue and contaminated water. Pyrolysis typically occurs under pressure and at operating temperatures above 430 °C (800 °F). The pyrolysis gases require further treatment. The off-gases may be treated in a secondary combustion chamber, flared, and partially condensed. Particulate removal equipment such as fabric filters or wet scrubbers are also required.

Conventional thermal treatment methods, such as rotary kiln, rotary hearth furnace, or fluidized bed furnace, are used for waste pyrolysis. Kilns or furnaces used for pyrolysis would be physically similar to the equipment described in the incineration, but would operate at lower temperature and with less air supply than would be required for combustion. Molten salt process may also be used for waste pyrolysis.

2.4 PYROLYSIS AND GASIFICATION OF SEWAGE SLUDGE

Sewage sludge production has been increasing due to the growth of urban wastewater treatment plants in particular in Poland and eastern Europe. Therefore, sludge disposal is one of the most important task. Agricultural use of sewage sludge and disposal through land filling is expected to decrease due to administrative, legal control restriction in EU. New European legislation prohibits a disposal of waste with >5% organic carbon after 2005. Recently, European water companies rethink their approach to sewage sludge regarding it as a sustainable energy resource. Thermal processing of sewage sludge including drying, pyrolysis and gasification or combustion may be an alternative to other ways of its utilisation.

In order to asses possibilities of sewage sludge thermal utilisation and its energetic potential the thermogravimetric methods have been employed. Thermogravimetric analysis (TGA) provides a rapid method for determining the temperature-decomposition profile of a material and the kinetics of its thermal decomposition. The kinetics of biomass pyrolysis is of great importance in the context of chemical reactor engineering and energy recovery. Modelling the processes of pyrolysis of biomass requires kinetics of mass loss and gas evolving.

In the present work pyrolysis of municipal sludge (after anaerobic digestion) from the wastewater treatment plants (WTP) in city of Łódź and Częstochowa have been investigated by means of TGA, in the temperature range 30-1000°C. This test method covers determination of the kinetic parameters such as Arrhenius activation energy and pre-exponential factor for

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pyrolysis performed in the inert gas as well as for gasification carried out in a partially oxidising atmosphere (CO_2 , or H_2O vapour). The product - synthesis gas increased substantially amount of gases evolved during pyrolysis.

Moreover, the pyrolysis of sewage sludge and gasification of pyrolysis char was performed batch wise and continuously in lab scale reactors of various configurations. Elemental analysis of substrate and liquid and solid products was performed. Contents of evolved gases were analysed by gas chromatography. The mass balance of the process carrying out in the reactors was checked and the impact of process conditions on the yield of pyrolysis and gasification products was determined.

2.5 Pyrolysis and oil from sludge (OFS) processes

Pyrolysis is a thermal decomposition of organic substances in the absence of oxygen at temperatures ranging between 300 and 900°C.

It consists of a series of complex chemical reactions which lead to the decomposition and breakage of the organic matter and the separation of different components into individual gases. The products of the pyrolysis are pyrolysis gas, char and oil. The gas can be used as fuel, the char can also be burnt as fuel or disposed of, whereas the oil can be used as raw material for chemical industries or fuel.

Much attention has been given to the oil product from the pyrolysis of sewage sludge, the so-called oil from sludge (OFS) process. OFS is a two-stage process whereby pre-dried sewage sludge is heated at higher temperatures in the absence of oxygen and at pressures higher than the atmosphere, resulting in the conversion of the organic matter of the sludge to a

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vapour state. Through catalytic reactions in the presence of char, these vapours are converted to hydrocarbons.

The high content of silicate and copper in the sludge provides an additional catalyst for the reaction. The oil obtained has a high viscosity and high heating values of 29–38 MJ/kg.

The elementary characteristics of the oil are reported to be generally stable over a wide range of operating conditions. Typical values for C, H, O, N and S are 76, 11, 6.5, 4 and 0.5%, respectively. In terms of its carbon content (70–80%), the oil corresponds to that of heavy crude oil. The advantages mentioned for this process include the reduction of sewage sludge to a small volume of inert residue, the production of a high quality oil which can be used in various chemical processes, the exclusion of the formation of harmful by-products, e.g. tars and dioxins, due to low operation temperatures and the binding of heavy metals mainly in the by-products. The successful development of the OFS process was started by the Environmental Canada Wastewater Technology Centre in Canada in 1982, based on the research originally carried out at Tübingen University in Germany. The Tübingen process was carried out at a low temperature of around 300°C and produced 20–30% oil per kg of dry sludge. Other groups who have been involved include: Hamburg University, Germany; University of Waterloo, Canada and University of Brussels, Belgium. Kyriakos undertook a comparison of their results and compiled details of the experiments (Table 2.8).

Table 2.8 Comparison of oil yields (kg/kg daf sludge) from various groups [16]

| Pressure temp, °c | Tubingen university | Environmental Canada | Hamburg university | University of Waterloo | University of Brussels |
|-------------------|---------------------|----------------------------------|--------------------|------------------------|----------------------------------|
| 300 | 25 ^a -40 | ---- | 25 ^b | ---- | 16 ^c -18 ^d |
| 350 | ---- | 18 ^e | ---- | 41 ^f | 24 ^c -39 ^d |
| 400 | ---- | ---- | 38 ^b | 52 ^f | ---- |
| 450 | ---- | 32 ^e -36 ^g | ---- | 52 ^f | 30 ^c -41 ^d |
| 500 | ---- | ---- | 42 ^b | 47 ^f | ---- |
| 600 | ---- | ---- | 24-42 ^b | 39 ^f | ---- |
| 700 | ---- | ---- | 24-42 ^b | 20 ^f | ---- |

^aDependent on origin of sludge.

^bLaboratory fluidized bed.

^cMeasured in lab. Fluidized bed.

^dIf unaccounted for, equal to oil.

^eSmall batch units.

^fSmall bench fluidized bed.

^gContinuous laboratory unit.

CHAPTER 3

EXPERIMENTAL DETAILS

3.1 The chemicals used in the experiment

3.1.1 The fine dried sewage sludge

Sewage sludge samples were collected in different places and time. They were used in this experiment and are shown in Table 3.1.

Table 3.1 List of source of samples

| Sample Number | Source of sample | Acquired date |
|---------------|---|----------------|
| 9 – 02 | Rattanakosin Water Quality Controlling Unit | September 2003 |
| 8 – 11 | Ayudhaya Hospital | August 2003 |
| 8 – 10 | Waste water Treatment Unit of Ramindra Government Community | August 2003 |
| M – 11 | Patumthani Hospital | March 2003 |
| 9 – 12 | Central Waste water Treatment Unit of Sahapattana Company | September 2003 |

3.2 Instruments

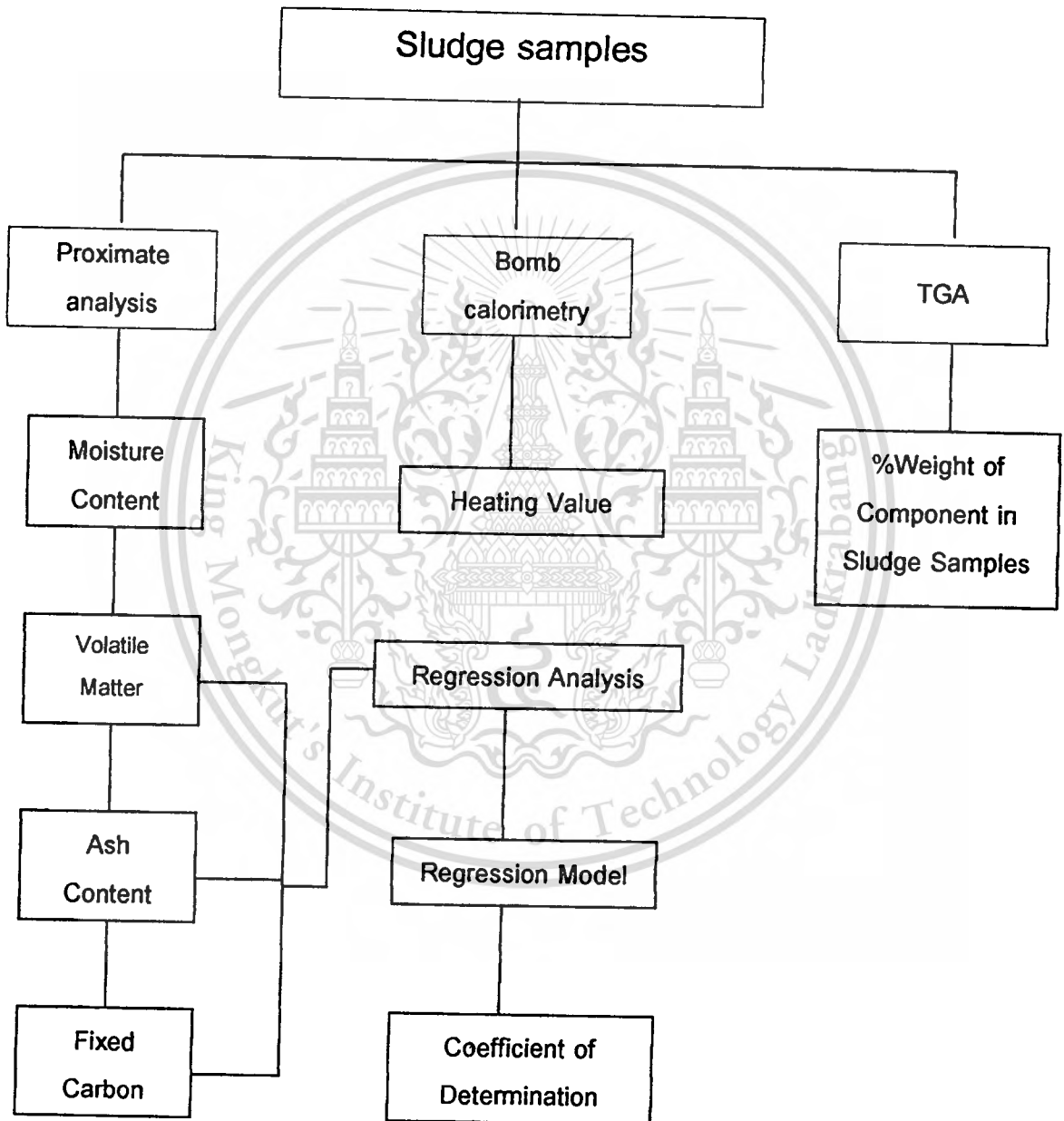
Lists of instrument are shown in Table 3.2

Table 3.2 Lists of instrument

| Instrument | Model |
|---|------------------------------------|
| Automatic Bomb Calorimeter | Gallenkamp PLC (Sanyo) |
| Thermogravimetric Analysis (TGA) | Pyris 1 TGA (Perkin Elmer) |
| Furnace | CSF 1200 (Carbolite Furnace) |
| Drying Oven | Moisture Oven Type |
| Capsules with cover (using in determining moisture) | Stainless Type |
| Electric Muffle Furnace | EF-220 (Contour Lamer Company) |
| Capsules | Porcelain |
| Balance | TC-254 (Denver Instrument Company) |
| Crucible Cover | Platinum Type |
| Crucible | Platinum Type |
| Vertical Electric Tube Furnace | Nova TF7 (Mccrelly co. limited) |
| Nitrogen gas tanks | TIG (Thai Industrial Gas) Company |
| Hoses | Rubber Type |
| Cotton Rope | 7 cm of length |
| Desiccators | Glass Type |
| Firing Wire | 9 cm of length |

3.3 Flow chart of experiment

This experiment investigated sludge samples in many aspects. It could be shown as following flow chart.



3.4 Sewage sludge composition analysis

The composition analysis of the sewage sludge was used to determine decomposition behavior of heat, calorific value, moisture, volatile matter and fixed carbon of sewage sludge as shown in Table 3.3

Table 3.3 The analysis method of the sewage sludge composition

| The analysis composition | The analysis method |
|--------------------------------|-----------------------------------|
| Decomposition Behavior of Heat | Thermogravimetric Analysis Method |
| Calorific Value | Bomb Calorimetry method |
| Volatile Content | ASTM D 3175 |
| Fixed Carbon Content | ASTM D 3174 |
| Ash Content | ASTM D 3174 |
| Moisture Content | ASTM D 3173 |

3.5 Characterization of Sewage Sludge

3.5.1 Moisture content in sewage sludge: ASTM D 3173

Put watch glass into oven at temperature of 110 °C for 30 minutes. Let it cool down, then weighed and recorded it. Took 1 gram of sewage sludge into the watch glass and dried it in oven at temperature of 105 to 110 °C for 1 hour. After it cooled, weighed and recorded. Moisture content can be calculated as follows:

$$M = \frac{(W_1 - W_2) \times 100}{W}$$

Where M = Moisture content percentage

W_1 = Sewage sludge including watch glass's weight before burning (g)

W_2 = Sewage sludge including watch glass's weight after burning (g)

W = Sewage sludge's weight (g)

3.5.2 Ash content in sewage sludge: ASTM D 3174

Burned porcelain crucible with its lid in furnace at temperature of 750 °C for 1 hour. Allowed it to cool down in desiccators and then weighed. Took 1 gram of sewage sludge into the crucible, then repeated burning in the furnace at same temperature for 2 hours and allowed it to cool down. Put it in the deccicator and weighed it with its lid. Recorded all data. Ash content can be calculated as follows:

$$A = \frac{(W_3 - W_4) \times 100}{W}$$

Where A = Ash content percentage
 W_3 = Weight of ash including crucible and its lid (g)
 W_4 = Weight of crucible and its lid (g)
 W = Ash weight (g)

3.5.3 Volatile matter content in sewage sludge: ASTM D 3175

Burned nickle crucible with its lid in the furnace at temperature of 950 °C for 30 minutes then took it out and allowed it to cool down in the deccicator, weighed and recorded data. Put 1 gram of sewage sludge into the nickle crucible and closed it with its lid. Heated at temperature of 300 °C for 3 minutes, at temperature of 600 °C for 10 minutes, and finally at temperature of 950 °C for 6 minutes, respectively. Took it out and allowed it to cool down at room temperature. Put it into the deccicator for 5 minutes, weighed and recorded the data. Volatile matter content can be calculated as follows:

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$$V = \frac{[(W_5 - W_6) \times 100] - M}{W}$$

- Where V = Volatile content percentage
- M = Moisture percentage
- W_5 = Weight of crucible with its lid including sewage sludge before burning (g)
- W_6 = Weight of crucible with its lid including sewage sludge after burning (g)
- W = Weight of sewage sludge (g)

3.5.4 Fixed carbon content in the sewage sludge : ASTM D 3174

After the results of moisture content, ash content and volatile content were achieved, the fixed carbon content would be calculated from these data as follows:

$$\text{Fixed carbon percentage} = 100 - \text{Moisture \%} - \text{Ash \%} - \text{Volatile \%}$$

3.5.5 Sulfur content and heat of combustion in sewage sludge

1 gram of sewage sludge was operated in bomb calorimeter. After temperature in bomb calorimeter was to the highest point and constant. Recorded initial and final temperature. Adjusted pH by NH_4OH and filled with hot water to 250 ml. Dropped 1 ml of HCl 1:1. Boiled it for 15 minutes and put 10 ml of BaCl_2 while it was boiling. After that, it was left for 2 hours. Filtrated it by No.42 filtered paper. Then weighed and recorded porcelain crucible and put the filtered paper into it. After that, they were burned by using Bunsen lamb and then put them in oven at 800°C for 2 hours. Put porcelain crucible into the desiccators to cool down. Weighed porcelain crucible with filtered paper and recorded the data. Sulfur content was calculated as follows:

$$\% \text{ Sulfur in the analysis sample} = \frac{(\text{Weight BaSO}_4)(13.738)}{\text{sample weight}}$$

And gross heat of combustion was calculated as follows:

$$\text{Gross heat of combustion (cal/g)} = [(\Delta T)(W) - e_1 - e_2 - e_3 - e_4]$$

- where ΔT = Increased temperature ($T_2 - T_1$) ($^\circ\text{C}$)
 W = Energy equivalent of calorimeter ($\text{cal}/^\circ\text{C}$)
 = 2500 $\text{cal}/^\circ\text{C}$
 e_1 = Heat value correction of the construction of HNO_3 (cal)
 = 1.4 x ml of 0.0725 N Na_2CO_3

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$$\begin{aligned}
 e_2 &= \text{Heat value correction of the construction of H}_2\text{SO}_4 \text{ (cal)} \\
 &= 22.6 \times (\%S) \\
 e_3 &= \text{Heat value correction of the wire (cal)} \\
 &= (335 \times 2.479 \times 10^{-3}) \text{ (length of burnt wire)} \\
 e_4 &= \text{Heat value correction of the cotton rope (cal)} \\
 &= (4180 \times 8.80 \times 10^{-3}) \text{ (length of burnt cotton rope)}
 \end{aligned}$$

3.5.6 Decomposition Analysis by TGA Method

Weighed 20 mg of sewage sludge. Put it into furnace and heated it from 25 °C to 105 °C with heating rate 25 °C/minute. Hold for 12 minutes at temperature of 105 °C. Then heated from temperature of 105 °C to 800 °C with heating rate 20 °C/minute to determine the composition of sewage sludge and then printed the results. Conditions used in this analysis were reasonable as shown in Table 3.4.

Table 3.4 Appropriate processing conditions of Thermogravimetric Analysis Method

| TEMP(°C) | | RATE (°C/min) | REASON |
|----------|-------|------------------|---|
| INITIAL | FINAL | | |
| 25 | 105 | 25 | - To evaporize water in sample |
| 105 | - | - | - Hold for 12 minutes to eliminate excess water |
| 105 | 800 | 20 | - To determine the decomposition of the sewage sludge |

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3.6 Regression Analysis

Results given from Proximate Analysis and Bomb Calorimeter were used to estimate regression models and determine the coefficient of determination (R^2).



CHAPTER 4

RESULTS AND DISCUSSIONS

From the research project "Correlation between Heating value and Proximate Analysis of Sewage Sludges". Firstly, we determined the properties of sludge samples by proximate analysis method, bomb calorimetry method, and thermo gravimetric analysis (TGA). Secondly, we analyzed the results using a linear regression analysis. Finally, we discussed the results of each sludge sample after being analyzed.

4.1 Results from proximate analysis

Proximate analysis is used for determination of composition of sewage sludge. The results are shown in Table 4.1.

Table 4.1 Proximate analysis of sewage sludge studied

| Sludge Sample | Moisture ASTM D 3173 (wt%) | Volatile Matter ASTM D 3175 (wt%) | Ash ASTM D 3174 (wt%) | Fixed Carbon ASTM D 3174 (wt%) |
|---------------|----------------------------------|---|-----------------------------|--------------------------------------|
| 1 | 5.51 | 33.31 | 55.42 | 5.76 |
| (9 - 12) | Dry basis | 35.25 | 58.65 | 6.1 |
| 2 | 4.74 | 37.61 | 53.18 | 4.47 |
| (8 - 11) | Dry basis | 39.49 | 55.83 | 4.68 |
| 3 | 4.69 | 29.95 | 59.16 | 6.2 |
| (8 -10) | Dry basis | 31.42 | 62.07 | 6.51 |
| 4 | 6.34 | 49.87 | 32.9 | 10.89 |
| (m11) | Dry basis | 53.25 | 35.13 | 11.62 |
| 5 | 2.53 | 33.61 | 61.75 | 2.11 |
| (9 - 02) | Dry basis | 34.48 | 63.35 | 2.17 |

NOTE; dry basis means the classified without moisture.

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From Table 4.1, the compositions of sewage sludge were determined based on as-received and dry bases. The sludge sample 5 (9-02) had the lowest moisture and fixed carbon compared to the sludge sample 4 (m11) that had the highest moisture, fixed carbon and volatile matter but the lowest ash.

4.2 Results from bomb calorimetry

A bomb calorimeter was used to determine heating values of sewage sludge. The results are shown in Table 4.2.

Table 4.2 Heating values of sludge sample by bomb calorimetric method

| Sludge Sample | Heating Value (kcal / kg) |
|---------------|---------------------------|
| 1(9 - 12) | 2,054.42 |
| 2(8 - 11) | 1,557.51 |
| 3(8 - 10) | 2,198.13 |
| 4(m11) | 2,571.36 |
| 5(9 - 02) | 1,654.16 |

The heating value of sludge sample 4 (m11) is the highest value (2571.36 kcal / kg) and that of sludge sample 2(8-11) is the lowest one.

4.3 Regression analysis

From proximate analysis method and bomb calorimetry method, we knew components of sludge samples and heating value as shown in Table 4.1 and Table 4.2, respectively. Therefore, we required to study the relationship between heating value and components of sludge samples by using regression analysis to determine the coefficient of determination (R^2) and

estimated regression model of each correlation which was related to heating value and volatile matter, heating value and ash, heating value and fixed carbon, heating value and volatile matter and fixed carbon, heating value and volatile matter and ash, heating value and ash and fixed carbon. Because heating value can explain many parameters such as volatile matter, ash, fixed carbon. Then we made the comparison and conclusion.

4.3.1 Linear regression of heating value vs. volatile matter

From Table 4.1 and Table 4.2, we could estimate regression model and determine the coefficient of determination (R^2) as follows:

The Simple Regression Model can be written as

$Y = a + bX_1$; where Y = Heating value, a and b = constants and X_1 = Volatile matter, resulting that

$$Y = 983.095 + 26.407(X_1)$$

$$R^2 = 0.3008$$

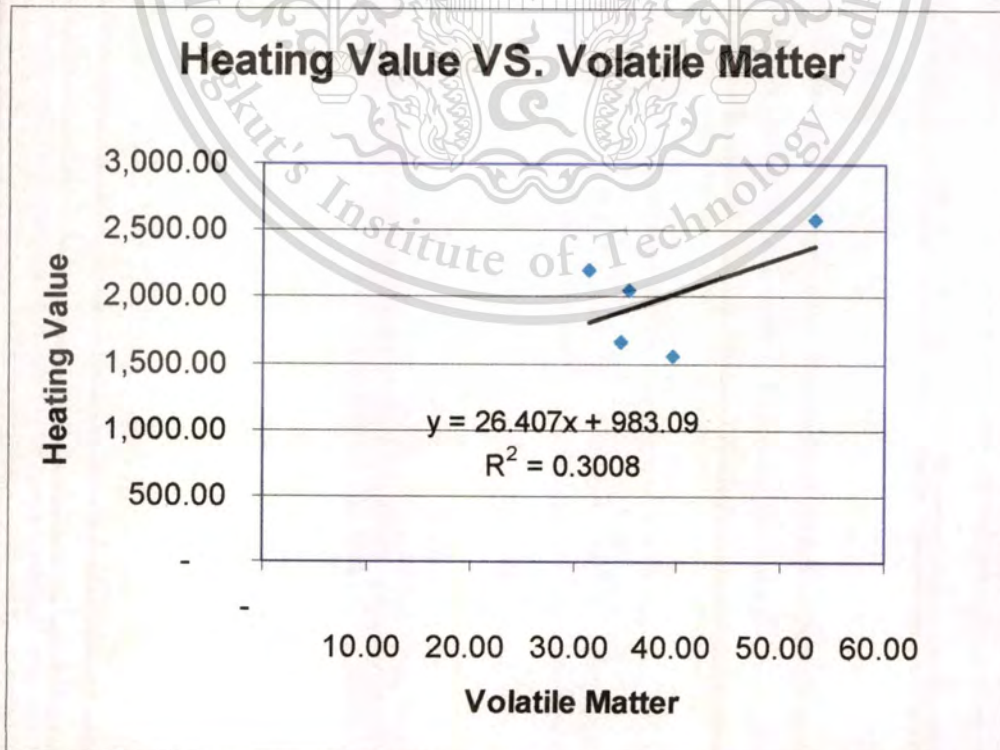


Figure 4.1 Linear Regression between Heating Value and Volatile Matter.

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It was observed that, heating value seems not to strongly correlate with volatile matter because the coefficient of determination (R^2) was only 0.3008. The other factors such as ash and fixed carbon might be further exploited.

4.3.2 Linear regression of heating value vs. ash

From Table 4.1 and Table 4.2, we could estimate regression model and determine the coefficient of determination (R^2) as follows:

The Simple Regression Model can be written as

$Y = a + bX_2$; where Y = Heating value, a and b = constants and X_2 = ash, resulting that

$$Y = 3360.976 - 24.613(X_2)$$

$$R^2 = 0.468$$

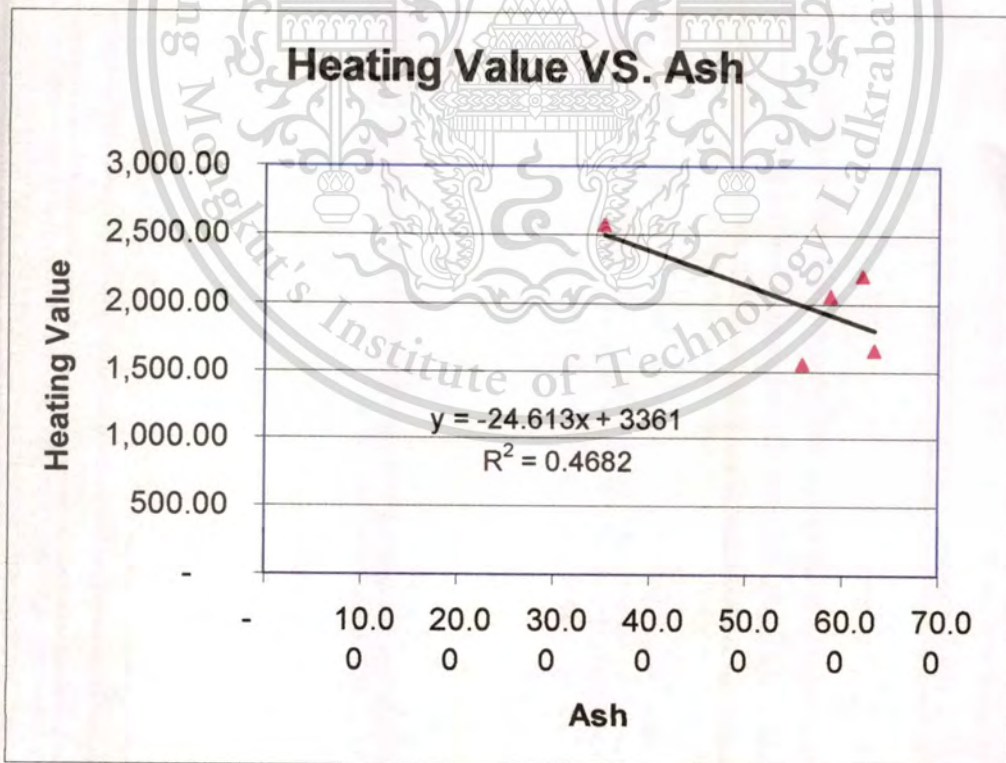


Figure 4.2 Linear Regression between Heating Value and Ash.

It was observed that, heating value seems not to strongly correlate with ash either because the coefficient of determination (R^2) was only 0.468. The other factor such as fixed carbon might be further exploited.

4.3.3 Linear regression line of heating value vs. fixed carbon

From Table 4.1 and Table 4.2, we could estimate regression model and determine the coefficient of determination (R^2) as follows:

The Simple Regression Model can be written as

$Y = a + bX_3$; where $Y =$ Heating value, a and $b =$ constants and $X_3 =$ Fixed carbon, resulting that

$$Y = 1331.777 + 108.645(X_3)$$

$$R^2 = 0.829$$

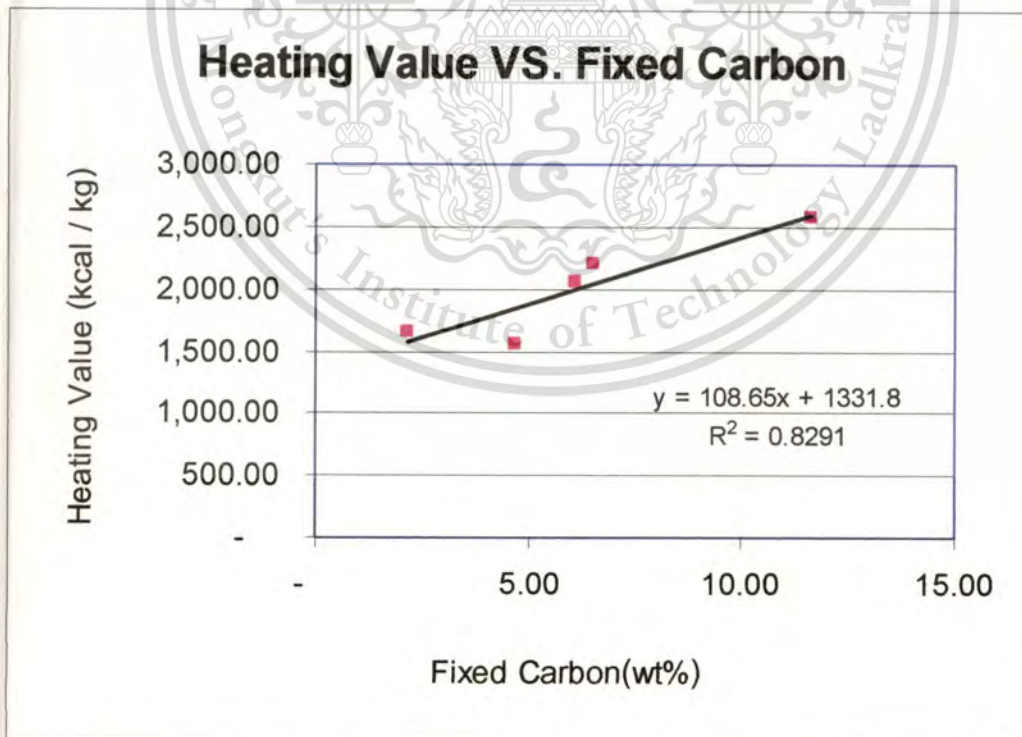


Figure 4.3 Linear Regression line between Heating Value and Fixed carbon.

It was observed that, heating value seems to strongly correlate with fixed carbon because the coefficient of determination (R^2) was 0.829. Three parameters (volatile matter, ash and fixed carbon) were dominant.

4.3.4 Multiple regression analysis of heating value vs. volatile matter and fixed carbon

From Table 4.1 and Table 4.2, we could estimate regression model and determine the coefficient of determination (R^2) as follows:

The Multiple Regression Model can be written as

$Y = a + bX_1 + cX_3$; where Y = Heating value, a , b and c = constants and X_1 = Volatile matter, X_3 = Fixed Carbon, resulting that

$$Y = 51.74 + 40.03(X_1) + 64.82(X_3)$$

$$R^2 = 0.973$$

It was observed that, heating value seems to strongly correlate with volatile matter and fixed carbon because the coefficient of determination (R^2) was 0.973. It was indicated that both volatile matter and fixed carbon were related together.

4.3.5 Multiple regression analysis of heating value vs. volatile matter and ash

From Table 4.1 and Table 4.2, we could estimate regression model and determine the coefficient of determination (R^2) as follows:

The Multiple Regression Model can be written as

$Y = a + bX_1 + cX_2$; where Y = Heating value, a , b and c = constants and X_1 = Volatile matter, X_2 = Ash, resulting that

$$Y = 5.5076 + 40.01(X_1) + 7.90(X_2)$$

$$R^2 = 0.974$$

It was observed that, heating value seems to strongly correlate with volatile matter and ash because the coefficient of determination (R^2) was 0.974 that was better relation than heating value and volatile matter and fixed carbon.

4.3.6 Multiple regression analysis of heating value vs. ash and fixed carbon

From Table 4.1 and Table 4.2, we could estimate regression model and determine the coefficient of determination (R^2) as follows:

The Multiple Regression Model can be written as

$Y = a + bX_2 + cX_3$; where Y = Heating value, a , b and c = constants and X_2 = Ash, X_3 = Fixed Carbon, resulting that

$$Y = -0.4766 + 18.22(X_2) + 161.74(X_3)$$

$$R^2 = 0.996$$

It was observed that, heating value seems to strongly correlate with ash and fixed carbon because the coefficient of determination (R^2) was 0.996. It pointed out that heating value and ash and fixed carbon were the best multiple regression model.

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The regression analysis model for parameter correlation were summarized in Table 4.3

Table 4.3 Summary six regression model and the coefficient of determination (R^2)

| Correlation | Model Regression | Coefficient of determination R^2 |
|------------------------|---|------------------------------------|
| H.V. and V.M. | $Y = 983.09 + 26.407(\text{Volatile matter})$ | 0.3008 |
| H.V. and Ash | $Y = 3360.976 - 24.613(\text{Ash})$ | 0.468 |
| H.V. and F.C. | $Y = 1331.777 + 108.645(\text{Fixed carbon})$ | 0.829 |
| H.V. and V.M. and F.C. | $Y = 51.74 + 40.03(\text{V.M.}) + 64.82(\text{Fixed carbon})$ | 0.973 |
| H.V. and V.M. and Ash | $Y = 5.5076 + 40.01(\text{V.M.}) + 7.90(\text{Ash})$ | 0.974 |
| H.V. and Ash and F.C. | $Y = -0.4766 + 18.22(\text{Ash}) + 161.74(\text{Fixed carbon})$ | 0.996 |

Where: H.V. = Heating Value
 F.C. = Fixed carbon
 V.M. = Volatile matter

4.4 Thermogravimetric Analysis (TGA);

Thermogravimetric Analysis (TGA) is the method for study of changing in mass of a sample as a function of temperature. Sludge samples were characterized by a thermogravimetric analyzer to determine the composition of sludge samples.

4.4.1 Sludge sample 1 (9-12)

Sludge sample 1 (9-12) from Rattanakosin Water Quality Controlling Unit, when it was tested by TGA, is shown in Figure 4.4

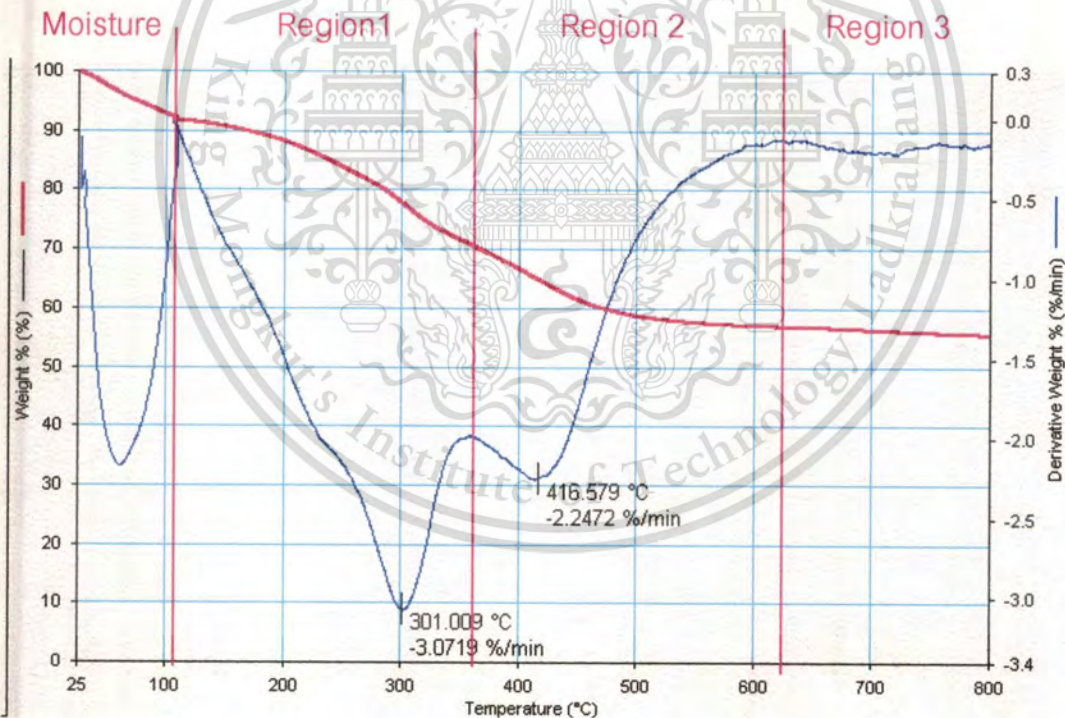


Figure 4.4 TGA thermograph of sludge sample 1 (9-12)

Figure 4.4 shows the TGA thermograph of sludge sample 1 (9-12). According to its derivatives, the weight loss can be divided into four regions namely moisture, region1, region2 and region3. Based on proximate analysis,

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regions 1 and 2 would correspond to volatile matters whereas region 3 would correspond to fixed carbon and ash content. Therefore, the weight loss at 105 °C corresponding to moisture in the sludge, account to be around 6%. Volatile matters (regions 1 and 2) account for 38%. The last region represents ash and fixed carbon accounted for 56%.

4.4.2 Sludge sample 2 (8-11)

Sludge sample 2 (8-11) from Ayudthaya Hospital, when it was tested by TGA, is shown in Figure 4.5

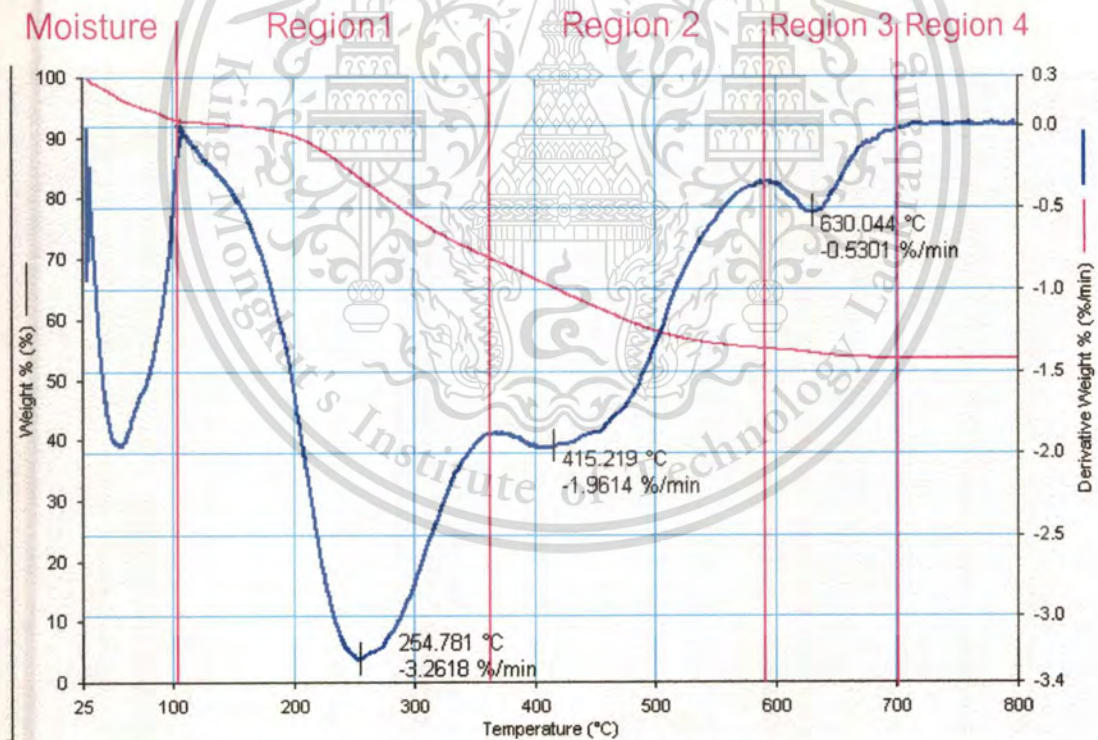


Figure 4.5 TGA thermograph of sludge sample 2 (8-11)

Figure 4.5 shows the TGA thermograph of sludge sample 2 (8-11). According to its derivatives, the weight loss can be divided into five regions namely moisture, region 1, region 2, region 3 and region 4. Based on proximate

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analysis, regions 1 to 3 would correspond to volatile matters whereas region 4 would correspond to fixed carbon and ash content. Therefore, the weight loss at 102 °C corresponding to moisture in the sludge, account to be around 5.5%. Volatile matters (regions 1 to 3) account for 41.5%. The last region represents ash and fixed carbon accounted for 53%.

4.4.3 Sludge sample 3 (8-10)

Sludge sample 3 (8-10) from Waste water Treatment Unit of Ramindra Government Community, when it was tested by TGA, is shown in Figure 4.6

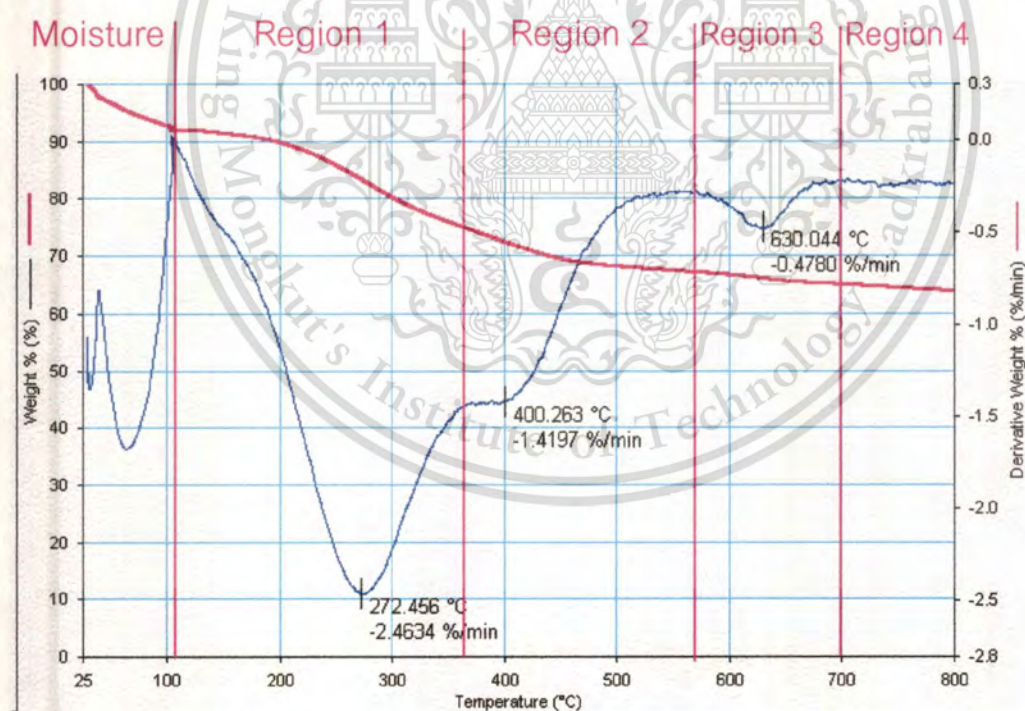


Figure 4.6 TGA thermograph of sludge sample 3 (8-10)

Figure 4.6 shows the TGA thermograph of sludge sample 3 (8-10). According to its derivatives, the weight loss can be divided into five regions namely moisture, region1, region2, region3 and region4. Based on proximate analysis, regions1 to 3 would correspond to volatile matters whereas region4 would correspond to fixed carbon and ash content. Therefore, the weight loss at 103°C corresponding to moisture in the sludge, account to be around 5.5%. Volatile matters (regions 1 to 3) account for 31.5%. The last region represents ash and fixed carbon accounted for 63%.

4.4.4 Sludge sample 4 (m11)

Sludge sample 4 (m11) from Patumthani, when it was tested by TGA, is shown in Figure 4.7

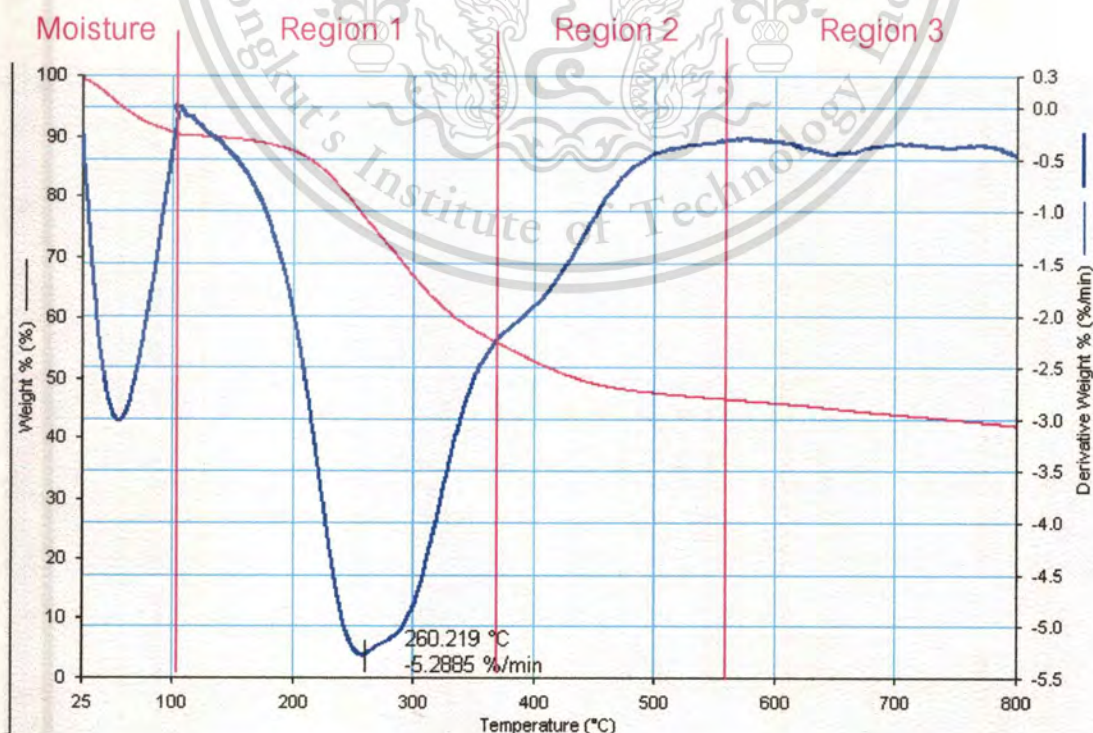


Figure 4.7 TGA thermograph of sludge sample 4 (m-11)

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Figure 4.7 shows the TGA thermograph of sludge sample 4 (m-11). According to its derivatives, the weight loss can be divided into four regions namely moisture, region1, region2 and region3. Based on proximate analysis, regions1 and 2 would correspond to volatile matters whereas region3 would correspond to fixed carbon and ash content. Therefore, the weight loss at 101°C corresponding to moisture in the sludge, account to be around 7.5%. Volatile matters (regions 1 and 2) account for 53%. The last region represents ash and fixed carbon accounted for 39.5%.

4.4.5 Sludge sample 5 (9-02)

Sludge sample 5 (9-02) from Central Waste Water Treatment Unit of Sahapattana Company, when it was tested by TGA, is shown in Figure 4.8

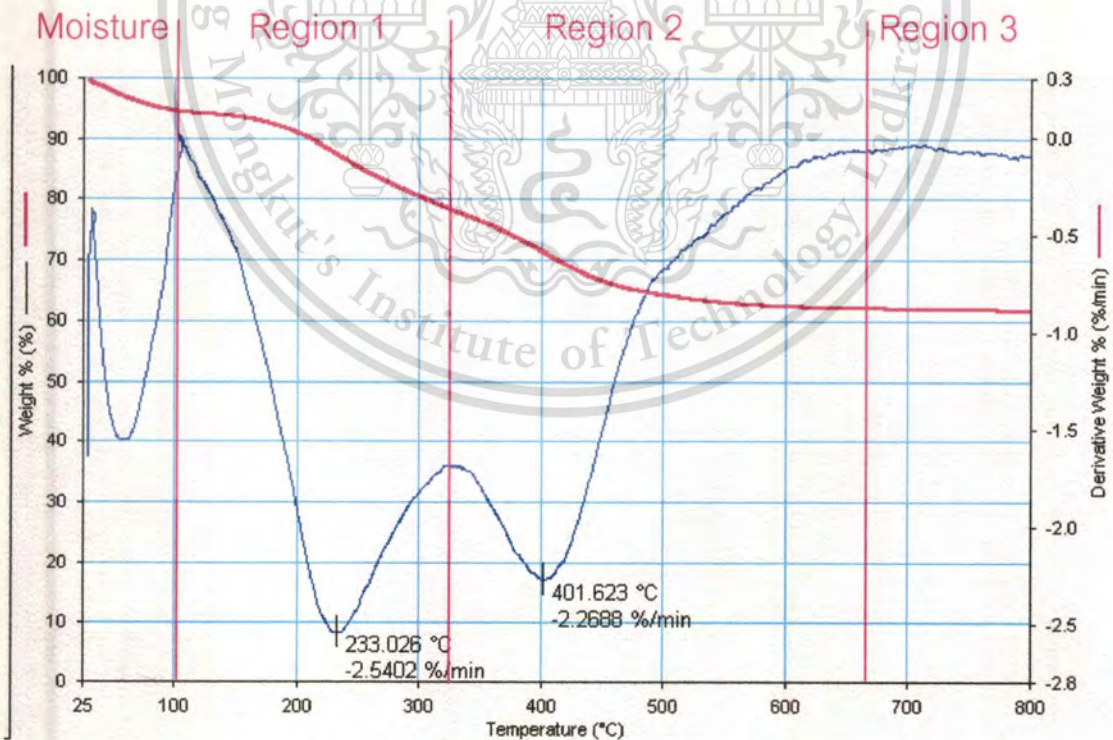


Figure 4.8 TGA thermograph of sludge sample 5 (9-02)

Figure 4.8 shows the TGA thermograph of sludge sample 5 (9-02). According to its derivatives, the weight loss can be divided into four regions namely moisture, region1, region2 and region3. Based on proximate analysis, regions1 and 2 would correspond to volatile matters whereas region3 would correspond to fixed carbon and ash content. Therefore, the weight loss at 103 °C corresponding to moisture in the sludge, account to be around 3%. Volatile matters (regions 1 and 2) account for 36%. The last region represents ash and fixed carbon account for 61%.

Thermogravimetric analysis data of each sewage sludge could be summerized in Table 4.4

Table 4.4 Summary of sludge samples from TGA

| Sludge Sample | Weight loss | | | | | | | | | |
|---------------|-------------|-----------------|------------|-----------------|------------|-----------------|------------|----------------|------------|------------|
| | Moisture | | Region1 | | Region2 | | Region3 | | Region4 | |
| | Temp (°C) | Wt % | Temp (°C) | Wt % | Temp (°C) | Wt % | Temp (°C) | Wt % | Temp (°C) | Wt % |
| 1(9-12) | 25 to 105 | 6 100-94 | 105 to 360 | 22 94-72 | 360 to 630 | 16 72-56 | 630 to 800 | 56 56-0 | - | - |
| 2(8-11) | 25 to 102 | 5.5 100-94.5 | 102 to 370 | 24.5 94.5-70 | 370 to 590 | 15 70-55 | 590 to 700 | 2 55-53 | 700 to 800 | 53 53-0 |
| 3(8-10) | 25 to 103 | 5.5 100-94.5 | 103 to 370 | 19.5 94.5-75 | 370 to 580 | 8 75-67 | 580 to 700 | 4 67-63 | 700 to 800 | 63 63-0 |
| 4(m11) | 25 to 101 | 7.5 100-92.5 | 101 to 370 | 36 92.5-56.5 | 370 to 550 | 17 56.5-39.5 | 550 to 800 | 39.5 39.5-0 | - | - |
| 5(9-02) | 25 to 103 | 3 100-97 | 103 to 325 | 18 97-79 | 325 to 670 | 18 79-61 | 670 to 800 | 61 61-0 | - | - |

Note : * Interval of weight loss

* Interval of temperature of that region

From Table 4.4, the sludge sample 5 (9-02) indicated the lowest moisture and fixed carbon when compared to the sludge sample 4 (m11) that showed the highest moisture, fixed carbon and volatile matters but the lowest ash.

Table 4.5 The percent deviation of moisture contents obtained between proximate analysis and TGA

| Sludge Sample | Moisture contents obtained by | | Deviation ¹ (%) |
|---------------|-------------------------------|---------------------------|-------------------------------|
| | Proximate analysis(wt%) | TGA (wt%) ² | |
| 1 (9-12) | 5.51 | 6 (25-105°C) ³ | 8.893 |
| 2 (8-11) | 4.74 | 5.5 (25-102°C) | 16.033 |
| 3 (8-10) | 4.69 | 5.5 (25-103°C) | 17.270 |
| 4 (m11) | 6.34 | 7.5 (25-101°C) | 18.296 |
| 5 (9-02) | 2.53 | 3 (25-103°C) | 18.577 |

Note;

1. % Deviation = $\left\{ \frac{(\text{Moisture contents from TGA} - \text{Moisture contents from Proximate analysis})}{\text{Moisture contents from Proximate analysis}} \right\} \times 100$
2. The number of moisture contents from TGA was derived from moisture region.
3. The temperature in parenthesis is a temperature account for moisture region from TGA.

Table 4.6 The percent deviation of volatile matters obtained between proximate analysis and TGA

| Sludge Sample | Volatile matters obtained by | | Deviation ¹ (%) |
|------------------|------------------------------|-----------------------------|-------------------------------|
| | Proximate analysis(wt%) | TGA (wt%) ² | |
| 1 (9-12) | 33.31 | 38 (105-630°C) ³ | 14.079 |
| 2 (8-11) | 37.61 | 41.5 (102-590°C) | 10.342 |
| 3 (8-10) | 29.95 | 31.5 (103-580°C) | 5.175 |
| 4 (m11) | 49.87 | 53 (101-550°C) | 6.276 |
| 5 (9-02) | 33.61 | 36 (103-670°C) | 7.111 |

Note ;

1. % Deviation = $\{(\bar{I} \text{ Volatile matter from TGA} - \text{Volatile matter from Proximate analysis}) / \text{Volatile matter from Proximate analysis}\} \times 100$
2. The number of volatile matter from TGA was derived from region 1, region 2 and region 3.
3. The temperature in parenthesis is (interval, boundary) temperature account for volatile product from TGA.

Table 4.7 The percent deviation of fixed carbon and ash contents obtained between proximate analysis and TGA

| Sludge Sample | Fixed carbon and Ash contents obtained by | | Deviation ¹ (%) |
|------------------|---|-----------------------------|-------------------------------|
| | Proximate analysis(wt%) | TGA (wt%) ² | |
| 1 (9-12) | 61.18 | 56 (630-800°C) ³ | 8.466 |
| 2 (8-11) | 57.65 | 53 (590-800°C) | 8.065 |
| 3 (8-10) | 65.36 | 63 (580-800°C) | 3.610 |
| 4 (m11) | 43.79 | 39.5 (550-800°C) | 9.796 |
| 5 (9-02) | 63.86 | 61 (670-800°C) | 4.478 |

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Note ;

1. % Deviation = $\frac{(|\text{Ash contents from TGA} - \text{Ash contents from Proximate analysis}|)}{\text{Ash contents from Proximate analysis}} \times 100$
2. The number of ash contents from TGA was derived from the last region.
3. The temperature in parenthesis is a temperature account for ash contents from TGA.

From Tables 4.5, 4.6, and 4.7 the percent deviations of moisture, volatile matters, and ash content obtained by between proximate analysis and TGA methods are not significantly different in each sludge sample. However, TGA is more convenient than proximate analysis by many reasons such that; it can provide all tested properties within a single run if altering an inert gas (N_2) to an oxidizing gas (O_2 or air) after its temperature is raised to and kept constant at $950^\circ C$. It also takes less time for obtaining the results than the proximate analysis method.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

We investigated five sludge samples that were collected from different places. We determined the compositions and the calorific value (heating value) by proximate analysis method, bomb calorimetry method and thermogravimetric analysis method. Then, the correlations between heating value and other properties (moisture, volatile matters, ash and fixed carbon) of sludge samples were obtained using a regression analysis. In this study, conclusions can be drawn as follows:

Sludge sample 4 (m11) obtained from Patumthani Hospital gave the highest volatile matters and heating value being 53.25wt% and 2571 kcal/kg, respectively.

The best regression model was correlation between heating value, ash and fix carbon because the coefficient of determination (R^2) was equal to 0.996. The best correlation is $H.V. = -0.4766 + 18.22Ash + 161.74F.C.$ (kcal/kg)

The behavior of the decomposition of sludge samples was investigated by TGA. We compared the experimental data of proximate analysis and TGA by calculation of percent deviations. The data are insignificantly different for each sludge sample.

It was found that, for the studied sludge samples, TGA could be used for determining the proximate analysis data (moisture, volatile matters, fixed carbon and ash content) within an acceptable accuracy.

5.2 Recommendations

From the research project, the results obtained were not sufficient to identify the substances in the sewage sludge. So, the sludge samples should be further analyzed by gas chromatography and mass spectroscopy techniques to identify those substances in order for the design of reactors.



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Abbreviations

1. BOD₅ 5- day biological oxygen demand
2. CEP catalytic extraction process
3. COD chemical oxygen demand
4. CFB circulating fluidized bed
5. C-G Carver-Greenfield process
6. d.m. dry mass
7. EU European Union
8. EW Etagenwirbler combustor
9. ESP electrostatic precipitator
10. FBC Fluidized bed combustor
11. HERS Hyperion energy recovery system
12. HTW high temperature Winkler process
13. MHF multiple hearth furnace
14. NIC newly industrialized countries
15. NL Netherlands
16. NJDEPE New Jersey Department of Environmental Protection and Energy
17. OFS oil from sludge process
18. PCDD chlorinated dibenzo-p-dioxins
19. PCDF chlorinated dibenzofurans
20. Pf pulverized fuel
21. RDF refuse-derived fuel
22. RCP recycled clean products process
23. SABS South American Bureau of Standard
24. SRVSA Somerset-Rarita Valley Sewerage Authority

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Abbreviations (continued)

25.SS suspended solids

26.STW sewage treatment work

27.SVZ Sekundarrohstoff Verwertungszenrum

28.t/a tons/annum

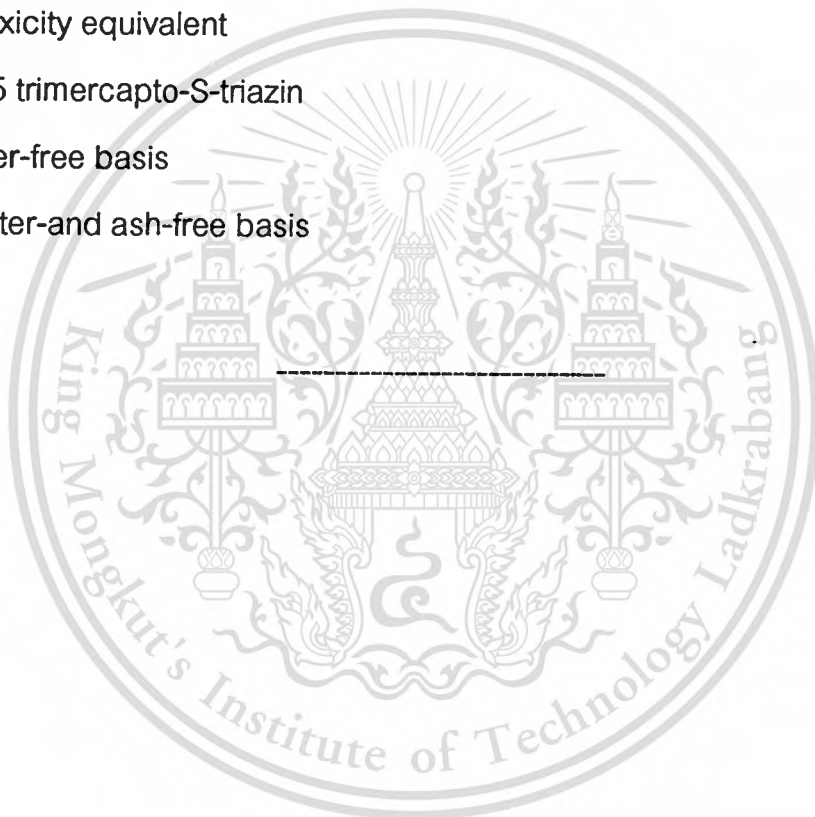
29.TBSA Two Bridges Sewerage Authority

30.TEG toxicity equivalent

31.TMT 15 trimercapto-S-triazin

32.wf water-free basis

33.waf water-and ash-free basis



The seal of King Mongkut's Institute of Technology Ladkrabang is a circular emblem. It features a central sunburst with rays emanating from a central point. Below the sunburst are two traditional Thai stupas (chedis) flanking a central, more ornate structure. The entire emblem is surrounded by a decorative border. The text "King Mongkut's Institute of Technology Ladkrabang" is inscribed around the perimeter of the seal.

Appendix B

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Linear Regression of Heating Value VS. Volatile

| | X | Y | X ² | XY | \hat{Y} | $(\hat{Y}-[\text{ave.}Y])^2$ | $(Y-[\text{ave.}Y])^2$ |
|----------------|----------|--------------|----------------|------------|-----------|------------------------------|------------------------|
| | 35.25 | 2,054.42 | 1,242.56 | 72,418.29 | 1,913.95 | 8,679.70 | 2,237.54 |
| | 39.49 | 1,557.51 | 1,559.46 | 61,506.26 | 2,025.92 | 353.51 | 202,142.07 |
| | 31.42 | 2,198.13 | 987.22 | 69,065.25 | 1,812.81 | 37,754.38 | 36,486.07 |
| | 53.25 | 2,571.36 | 2,835.56 | 136,925.03 | 2,389.28 | 146,051.11 | 318,372.51 |
| | 34.48 | 1,654.16 | 1,188.87 | 57,035.37 | 1,893.62 | 12,881.92 | 124,580.00 |
| Total | 193.89 | 10,035.58 | 7,813.67 | 396,950.20 | | 205,720.62 | 683,818.19 |
| Average | 38.78 | 2,007.12 | | | | | |
| Square | 1,503.73 | 4,028,518.33 | | | | | |

$$b = \frac{\sum xy - (n)(\text{ave.}X)(\text{ave.}Y)}{\sum x^2 - \frac{(\sum x)^2}{n}}$$

$$= 26.40729236$$

$$a = \text{ave.}Y - (b)(\text{ave.}X)$$

$$= 983.094937$$

Model $\hat{Y} = 983.094937 + 26.40729236(X_1)$

$$R^2 = \frac{\sum (\hat{Y} - [\text{ave.}Y])^2}{\sum (Y - [\text{ave.}Y])^2}$$

$$= 0.300841108$$

When ; $X_1 = X = \text{Volatile matter}$ $Y = \text{Heating Value}$

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Linear Regression of Heating Value VS. Ash

| | X | Y | X ² | XY | \hat{Y} | $(\hat{Y}-[ave.Y])^2$ | $(Y-[ave.Y])^2$ |
|----------------|----------|--------------|----------------|------------|-----------|-----------------------|-----------------|
| | 58.65 | 2,054.42 | 3,439.82 | 120,491.71 | 1,917.43 | 8,044.21 | 2,237.54 |
| | 55.83 | 1,557.51 | 3,116.99 | 86,956.05 | 1,986.84 | 411.32 | 202,142.07 |
| | 62.07 | 2,198.13 | 3,852.68 | 136,437.94 | 1,833.25 | 30,229.29 | 36,486.07 |
| | 35.13 | 2,571.36 | 1,234.12 | 90,331.95 | 2,496.32 | 239,323.10 | 318,372.51 |
| | 63.35 | 1,654.16 | 4,013.22 | 104,790.91 | 1,801.75 | 42,176.96 | 124,580.00 |
| Total | 275.03 | 10,035.58 | 15,656.84 | 539,008.56 | | 320,184.88 | 683,818.19 |
| Average | 55.01 | 2,007.12 | | | | | |
| Square | 3,025.66 | 4,028,518.33 | | | | | |

$$b = \frac{\sum xy - (n)(ave.X)(ave.Y)}{\sum x^2 - \sum ((n)(ave.X)^2)}$$

$$= -24.6129301$$

$$a = ave.Y - (b)(ave.X)$$

$$= 3360.975753$$

Model $\hat{Y} = 3360.975753 - 24.6129301(X_2)$

$$R^2 = \frac{\sum (\hat{Y} - [ave.Y])^2}{\sum (Y - [ave.Y])^2}$$

$$= 0.468231002$$

When; $X_2 = X = \text{Ash}$ $Y = \text{Heating Value}$

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Linear Regression of Heating Value VS. Fix Carbon

| X | Y | X ² | XY | \hat{Y} | $(\hat{Y}-[ave.Y])^2$ | $(Y-[ave.Y])^2$ |
|----------------|--------------|---------------------|---------------|------------------|-----------------------|-------------------|
| 6.10 | 2,054.42 | 37.21 | 12,531.96 | 1,994.51 | 158.83 | 2,237.54 |
| 4.68 | 1,557.51 | 21.90 | 7,289.17 | 1,840.24 | 27,848.71 | 202,142.07 |
| 6.51 | 2,198.13 | 42.38 | 14,309.83 | 2,039.06 | 1,020.28 | 36,486.07 |
| 11.62 | 2,571.36 | 135.02 | 29,879.23 | 2,594.24 | 344,709.53 | 318,372.51 |
| 2.17 | 1,654.16 | 4.71 | 3,589.52 | 1,567.54 | 193,229.91 | 124,580.00 |
| Total | 31.08 | 10,035.58 | 241.23 | 67,599.71 | 566,967.25 | 683,818.19 |
| Average | 6.22 | 2,007.12 | | | | |
| Square | 38.64 | 4,028,518.33 | | | | |

$$b = \frac{\sum xy - (n)(ave.X)(ave.Y)}{\sum x^2 - \sum ((n)(ave.X)^2)}$$

$$= 108.6453897$$

$$a = ave.Y - (b)(ave.X)$$

$$= 1331.777178$$

Model $\hat{Y} = 1331.777178 + 108.6453897(X)$

$$R^2 = \frac{\sum (\hat{Y}-[ave.Y])^2}{\sum (Y-[ave.Y])^2}$$

$$= 0.829119874$$

When; $X_3 = X = \text{Fixed Carbon}$ $Y = \text{Heating Value}$

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Multiple Regression of Heating Value VS. Volatile matter and F.C.

| | Z | X | Y | Z ² | X ² | Y ² | XZ | YZ | YX | (bX + cZ) ² |
|---------|-------|--------|-----------|----------------|----------------|----------------|----------|-----------|------------|------------------------|
| | 6.10 | 35.25 | 2,054.42 | 37.21 | 1,242.56 | 4,220,639.89 | 215.03 | 12,531.96 | 72,418.29 | 3,263,859.56 |
| | 4.68 | 39.49 | 1,557.51 | 21.90 | 1,559.46 | 2,425,852.35 | 184.81 | 7,289.17 | 61,506.26 | 3,550,647.76 |
| | 6.51 | 31.42 | 2,198.13 | 42.38 | 987.22 | 4,831,776.38 | 204.54 | 14,309.83 | 69,065.25 | 2,821,930.45 |
| | 11.62 | 53.25 | 2,571.36 | 135.02 | 2,835.56 | 6,611,902.54 | 618.77 | 29,879.23 | 136,925.03 | 8,323,469.95 |
| | 2.17 | 34.48 | 1,654.16 | 4.71 | 1,188.87 | 2,736,238.69 | 74.82 | 3,589.52 | 57,035.37 | 2,313,577.81 |
| Total | 31.08 | 193.89 | 10,035.58 | 241.23 | 7,813.67 | 20,826,409.85 | 1,297.97 | 67,599.71 | 396,950.20 | 20,273,485.53 |
| Average | 6.22 | 38.778 | 2,007.12 | 48.25 | 1,562.73 | | | | | |

$$b = \frac{(\sum Z^2)(\sum YX) - (\sum XZ)(\sum YZ)}{(\sum X^2)(\sum Z^2) - (\sum XZ)^2}$$

$$= 40.03$$

$$c = \frac{(\sum X^2)(\sum YZ) - (\sum XZ)(\sum XY)}{(\sum X^2)(\sum Z^2) - (\sum XZ)^2}$$

$$= 64.82$$

$$a = (\text{ave. } Y) - b(\text{ave. } X) - c(\text{ave. } Z)$$

$$= 51.741$$

$$\hat{Y} = 51.74103419 + 40.03(X_1) + 64.82(X_2)$$

$$R^2 = \frac{\sum (bX + cZ)^2}{\sum Y^2}$$

$$= 0.97345$$

When; X1 = X = Volatile matter

X3 = Z = Fixed carbon

Y = Heating Value

Multiple Regression of Heating Value VS. Volatile matter and Ash

| | Z | X | Y | Z ² | X ² | Y ² | XZ | YZ | YX | (bX + cZ) ² |
|---------|--------|--------|-----------|----------------|----------------|----------------|-----------|------------|------------|------------------------|
| | 58.65 | 35.25 | 2,054.42 | 3,439.82 | 1,242.56 | 4,220,639.89 | 2,067.41 | 120,491.71 | 72,418.29 | 3,563,891.94 |
| | 55.83 | 39.49 | 1,557.51 | 3,116.99 | 1,559.46 | 2,425,852.35 | 2,204.73 | 86,956.05 | 61,506.26 | 4,148,927.40 |
| | 62.07 | 31.42 | 2,198.13 | 3,852.68 | 987.22 | 4,831,776.38 | 1,950.24 | 136,437.94 | 69,065.25 | 3,097,851.93 |
| | 35.13 | 53.25 | 2,571.36 | 1,234.12 | 2,835.56 | 6,611,902.54 | 1,870.67 | 90,331.95 | 136,925.03 | 5,902,056.22 |
| | 63.35 | 34.48 | 1,654.16 | 4,013.22 | 1,188.87 | 2,736,238.69 | 2,184.31 | 104,790.91 | 57,035.37 | 3,586,634.79 |
| Total | 275.03 | 193.89 | 10,035.58 | 15,656.84 | 7,813.67 | 20,826,409.85 | 10,277.36 | 539,008.56 | 396,950.20 | 20,299,362.29 |
| Average | 55.01 | 38.778 | 2,007.12 | 3,131.37 | 1,562.73 | | | | | |

$$b = \frac{(\sum Z^2)(\sum YX) - (\sum XZ)(\sum YZ)}{(\sum X^2)(\sum Z^2) - (\sum XZ)^2}$$

$$= 40.41$$

$$c = \frac{(\sum X^2)(\sum YZ) - (\sum XZ)(\sum XY)}{(\sum X^2)(\sum Z^2) - (\sum XZ)^2}$$

$$= 7.90$$

$$a = (\text{ave.}Y) - b(\text{ave.}X) - c(\text{ave.}Z)$$

$$= 5.50761$$

$$\hat{Y} = 5.5076 + 40.41(X_1) + 7.90(X_2)$$

$$R^2 = \frac{\sum (bX + cZ)^2}{\sum Y^2}$$

$$= 0.97469$$

When; X₁ = X = Volatile matter

X₂ = Z = Ash

Y = Heating Value

Multiple Regression of Heating Value VS. Ash and F.C.

| | Z | X | Y | Z ² | X ² | Y ² | XZ | YZ | YX | (bX + cZ) ² |
|---------|-------|--------|-----------|----------------|----------------|----------------|----------|-----------|------------|------------------------|
| | 6.10 | 58.65 | 2,054.42 | 37.21 | 3,439.82 | 4,220,639.89 | 357.77 | 12,531.96 | 120,491.71 | 4,223,954.43 |
| | 4.68 | 55.83 | 1,557.51 | 21.90 | 3,116.99 | 2,425,852.35 | 261.28 | 7,289.17 | 86,956.05 | 3,147,696.65 |
| | 6.51 | 62.07 | 2,198.13 | 42.38 | 3,852.68 | 4,831,776.38 | 404.08 | 14,309.83 | 136,437.94 | 4,769,211.47 |
| | 11.62 | 35.13 | 2,571.36 | 135.02 | 1,234.12 | 6,611,902.54 | 408.21 | 29,879.23 | 90,331.95 | 6,347,828.86 |
| | 2.17 | 63.35 | 1,654.16 | 4.71 | 4,013.22 | 2,736,238.69 | 137.47 | 3,589.52 | 104,790.91 | 2,265,700.37 |
| Total | 31.08 | 275.03 | 10,035.58 | 241.23 | 15,656.84 | 20,826,409.85 | 1,568.81 | 67,599.71 | 539,008.56 | 20,754,391.78 |
| Average | 6.22 | 55.006 | 2,007.12 | 48.25 | 3,131.37 | | | | | |

$$b = \frac{(\sum Z^2)(\sum YX) - (\sum XZ)(\sum YZ)}{(\sum X^2)(\sum Z^2) - (\sum XZ)^2}$$

$$= 18.22$$

$$c = \frac{(\sum X^2)(\sum YZ) - (\sum XZ)(\sum XY)}{(\sum X^2)(\sum Z^2) - (\sum XZ)^2}$$

$$= 161.74$$

$$a = (\text{ave.}Y) - b(\text{ave.}X) - c(\text{ave.}Z)$$

$$= -0.47661$$

$$\hat{Y} = 18.22(X_2) + 161.74(X_3) - 0.4766$$

$$R^2 = \frac{\sum (bX + cZ)^2}{\sum Y^2}$$

$$= 0.996542$$

When; X₂ = X = Ash

X₃ = Z = Fixed Carbon

Y = Heating Value

Appendix C



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ตัวอย่างกากตะกอน

| ค.ย. | ครั้งที่ | น.น. ถ้วย | น.น. ตัวอย่าง | น.น. ถ้วย+ค.ย. หลงอบ | %ความชื้น | AVG แต่ละตัวอย่าง |
|------|----------|-----------|---------------|----------------------|-----------|-------------------|
| S1 | 1 | 20.1900 | 1.0009 | 21.1356 | 5.53 | 5.51 |
| | 2 | 21.2369 | 1.0000 | 22.1819 | 5.50 | |
| S2 | 1 | 20.7589 | 1.0002 | 21.7098 | 4.73 | 4.74 |
| | 2 | 20.9556 | 1.0002 | 21.9083 | 4.75 | |
| S3 | 1 | 20.9991 | 0.8549 | 21.8138 | 4.70 | 4.69 |
| | 2 | 21.2234 | 0.8336 | 22.0180 | 4.68 | |
| S4 | 1 | 19.8991 | 0.8639 | 20.5084 | 6.32 | 6.34 |
| | 2 | 21.5476 | 0.8674 | 22.3599 | 6.35 | |
| S5 | 1 | 19.3464 | 0.8477 | 20.1724 | 2.56 | 2.53 |
| | 2 | 19.5899 | 0.8395 | 20.3884 | 2.50 | |

| ค.ย. | ครั้งที่ | น.น. ถ้วย | น.น. ตัวอย่าง | น.น. ถ้วย+ค.ย. หลงอบ | %สารระเหย+ความชื้น | AVG แต่ละตัวอย่าง | %สารระเหย |
|------|----------|-----------|---------------|----------------------|--------------------|-------------------|-----------|
| S1 | 1 | 20.5082 | 0.9395 | 21.0808 | 38.84 | 38.82 | 33.31 |
| | 2 | 21.8630 | 0.9552 | 22.2476 | 38.80 | | |
| S2 | 1 | 21.2518 | 0.9501 | 21.7993 | 42.37 | 42.35 | 37.61 |
| | 2 | 21.4459 | 0.9512 | 21.9945 | 42.33 | | |
| S3 | 1 | 20.6074 | 0.8104 | 21.1372 | 34.62 | 34.64 | 29.95 |
| | 2 | 20.8543 | 0.8094 | 21.3832 | 34.66 | | |
| S4 | 1 | 20.2948 | 0.8063 | 20.6481 | 56.18 | 56.21 | 49.87 |
| | 2 | 21.4526 | 0.7569 | 21.7839 | 56.23 | | |
| S5 | 1 | 21.1831 | 0.8174 | 21.7052 | 36.13 | 36.15 | 33.61 |
| | 2 | 21.8843 | 0.8026 | 22.3967 | 36.16 | | |

| ค.ย. | ครั้งที่ | น.น. ถ้วย | น.น. ตัวอย่าง | น.น. ถ้วย+แก้ว | %แก้ว | AVG แต่ละตัวอย่าง |
|------|----------|-----------|---------------|----------------|-------|-------------------|
| S1 | 1 | 35.1966 | 1.0002 | 35.7510 | 55.43 | 55.42 |
| | 2 | 35.6284 | 1.0000 | 36.1805 | 55.41 | |
| S2 | 1 | 36.0771 | 1.0005 | 36.6089 | 53.15 | 53.18 |
| | 2 | 35.4184 | 1.0001 | 35.9505 | 53.20 | |
| S3 | 1 | 35.2522 | 0.4688 | 35.5295 | 59.15 | 59.16 |
| | 2 | 35.9636 | 0.4266 | 36.2160 | 59.17 | |
| S4 | 1 | 35.0830 | 0.7435 | 35.3274 | 32.87 | 32.90 |
| | 2 | 35.7326 | 0.7166 | 35.9685 | 32.92 | |
| S5 | 1 | 34.7666 | 0.8460 | 35.2892 | 61.77 | 61.75 |
| | 2 | 34.7452 | 0.8426 | 35.2653 | 61.73 | |

| %คาร์บอนคงตัว | S1 | S2 | S3 | S4 | S5 |
|---------------|------|------|------|-------|------|
| | 5.76 | 4.47 | 6.20 | 10.89 | 2.11 |

| | Moisture | Volatle | Ash | Fix carbon |
|-----------|----------|---------|-------|------------|
| S1 | 5.51 | 33.31 | 55.42 | 5.76 |
| Dry basis | 35.25 | 58.65 | 6.10 | |
| S2 | 4.74 | 37.61 | 53.18 | 4.47 |
| Dry basis | 39.49 | 55.83 | 4.68 | |
| S3 | 4.69 | 29.95 | 59.16 | 6.20 |
| Dry basis | 31.42 | 62.07 | 6.51 | |
| S4 | 6.34 | 49.87 | 32.90 | 10.89 |
| Dry basis | 53.25 | 35.13 | 11.62 | |
| S5 | 2.53 | 33.61 | 61.75 | 2.11 |
| Dry basis | 34.48 | 63.35 | 2.17 | |

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Results from bomb calorimetry method

Sample 1

- Weight of sample = 1.1271 g.

- Length of wire = 9 cm.

Weight of wire = 0.0212 g.

- Length of cotton = 7 cm.

Weight of cotton = 0.0090 g.

- Temp. 1 = 28.007 °C

- Temp. 2 = 28.852 °C

- Titrate by NaCO_3 = 4.1 ml.

After burn:

- Length of wire = 8.8 cm.

- Crucible + Cover = 45.1913 g.

- Crucible + Cover + Sample1 = 45.2442 g.

- Sample 1 = 0.0529 g.

$$\begin{aligned} \text{Gross heat of combustion (cal/g)} &= [(\Delta T) (W) - e_1 - e_2 - e_3 - e_4] \\ &= 2054.419 \text{ cal/g} \end{aligned}$$

Results from bomb calorimetry method

Sample 2

- Weight of sample = 1.0465 g.

- Length of wire = 9.2 cm.

Weight of wire = 0.0218 g.

- Length of cotton = 7 cm.

Weight of cotton = 0.0087g.

- Temp. 1 = 28.273 °C

- Temp. 2 = 28.918 °C

- Titrate by NaCO_3 = 5.4 ml.

After burn:

- Length of wire = 9.0 cm.

- Crucible + Cover = 35.1038 g.

- Crucible + Cover + Sample2 = 35.1403 g.

- Sample 2 = 0.0367 g.

$$\begin{aligned} \text{Gross heat of combustion (cal/g)} &= [(\Delta T) (W) - e_1 - e_2 - e_3 - e_4] \\ &= 1557.5148 \text{ cal/g} \end{aligned}$$

Results from bomb calorimetry method

Sample 3

- Weight of sample = 1.0026 g.

- Length of wire = 9.2 cm.

Weight of wire = 0.0237 g.

- Length of cotton = 7 cm.

Weight of cotton = 0.0057g.

- Temp. 1 = 27.084 °C

- Temp. 2 = 27.981 °C

- Titrate by NaCO_3 = 2.4 ml.

After burn:

- Length of wire = 9.0 cm.

- Crucible + Cover = 35.0810 g.

- Crucible + Cover + Sample3 = 35.1360 g.

- Sample 3 = 0.0550 g.

$$\begin{aligned} \text{Gross heat of combustion (cal/g)} &= [(\Delta T) (W) - e_1 - e_2 - e_3 - e_4] \\ &= 2198.1302 \text{ cal/g} \end{aligned}$$

Results from bomb calorimetry method

Sample 4

- Weight of sample = 1.0211 g.

- Length of wire = 9.2 cm.

Weight of wire = 0.0220 g.

- Length of cotton = 7 cm.

Weight of cotton = 0.0061g.

- Temp. 1 = 29.127 °C

- Temp. 2 = 30.175 °C

- Titrate by NaCO_3 = 8.5 ml.

After burn:

- Length of wire = 9.0 cm.

- Crucible + Cover = 35.0692 g.

- Crucible + Cover + Sample4 = 35.0330 g.

- Sample 4 = 0.0362 g.

$$\begin{aligned} \text{Gross heat of combustion (cal/g)} &= [(\Delta T) (W) - e_1 - e_2 - e_3 - e_4] \\ &= 2571.362 \text{ cal/g} \end{aligned}$$

Results from bomb calorimetry method

Sample 5

- Weight of sample = 1.0150 g.

- Length of wire = 9cm.

Weight of wire = 0.0209 g.

- Length of cotton = 7 cm.

Weight of cotton = 0.0058g.

- Temp. 1 = 28.249 °C

- Temp. 2 = 28.932 °C

- Titrate by NaCO_3 = 4.2 ml.

After burn:

- Length of wire = 8.8 cm.

- Crucible + Cover = 35.1566 g.

- Crucible + Cover + Sample5 = 35.0812 g.

- Sample 5 = 0.0754 g.

$$\begin{aligned} \text{Gross heat of combustion (cal/g)} &= [(\Delta T) (W) - e_1 - e_2 - e_3 - e_4] \\ &= 1654.158 \text{ cal/g} \end{aligned}$$