

**EGE UNIVERSITY**  
**SCIENTIFIC RESEARCH PROJECT REPORT**  
**PROJECT NO: 2003/MÜH/031**

**INVESTIGATION OF SUPERCRITICAL  
AND SOXHLET EXTRACTIONS  
OF SEWAGE SLUDGES**

**Tülay GÜNGÖREN**  
**Department of Chemical Engineering**  
**603.01.00**

**Supervised by: Prof. Dr. Mehmet SAĞLAM**  
**Assoc. Prof. Dr. Levent BALLİCE**

**Bornova – İzmir**

### III

Sayın Tülay GÜNGÖREN tarafından YÜKSEK LİSANS tezi olarak sunulan “Investigation of Supercritical and Soxhlet Extractions of Sewage Sludges” başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve 07.10.2004 tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

#### Jüri Üyeleri:

#### İmza

Jüri Başkanı : Prof. Dr. Mehmet SAĞLAM  
Raportör Üye: Prof. Dr. Mehmet SAĞLAM  
Üye : Prof. Dr. Mithat YÜKSEL  
Üye : Prof. Dr. Jale YANIK



**ÖZET**  
**ATIK ÇAMURLARIN KRİTİK ÜSTÜ VE SOXHLET EKSTRAKSİYONLARININ**  
**İNCELENMESİ**

GÜNGÖREN, Tülay

Yüksek Lisans Tezi, Kimya Mühendisliği Bölümü

Tez Yöneticileri: Prof. Dr. Mehmet Sağlam

Doç. Dr. Levent Ballice

Eylül 2004, 169 sayfa

Bu çalışmada, Petkim Petrokimya Kompleksi atıksu arıtma tesisinde arıtma işlemi sonrası elde edilen atık çamurların Soxhlet ve kritik üstü koşullarda su ve toluen ekstraksiyonu yöntemiyle sıvılaştırılması incelenmiştir. Bu çalışma kapsamında, maksimum ekstraksiyon verimi ve buna bağlı olarak organik madde dönüşümü belirlenmiştir. En uygun reaksiyon koşulları saptanmış olup elde edilen ürünlerin farklı yöntemlerle karakterizasyon işlemi gerçekleştirilmiştir.

Çözgen tipi, çözgen/katı oranı ve sıcaklık gibi parametreler incelenerek maksimum organik madde dönüşümünün sağlandığı optimum reaksiyon koşulları tespit edilmiştir.

**Anahtar sözcükler:** Kritik Üstü Akışkan Ekstraksiyonu, Soxhlet Ekstraksiyonu, Kolon Kromatografisi, Atık Çamur



## VII

### **ABSTRACT** **INVESTIGATION OF SUPERCRITICAL** **AND SOXHLET EXTRACTIONS** **OF SEWAGE SLUDGES**

GÜNGÖREN, Tülay

MSc in Chemical Engineering

Supervisors: Prof. Dr. Mehmet Sağlam

Assoc. Prof. Dr. Levent Ballice

September 2004, 169 pages

In this study, liquefaction of sewage sludges obtained from Wastewater Treatment Plant of Petkim Petrochemical Complex by Soxhlet and supercritical water and toluene extractions were investigated. The scope of this work was to identify maximum extract yield which is related with recovery of organic matter in sewage sludge. The most suitable reaction conditions were determined and different techniques were used to characterize extraction products.

Some parameters like solvent type, solvent/solid ratio and temperature were investigated to determine the optimum reaction conditions for the maximum recovery of organic matter.

**Keywords:** Supercritical Fluid Extraction, Soxhlet Extraction, Column Chromatography, Sewage Sludge

## **IX**

### **ACKNOWLEDGEMENT**

Firstly, I would sincerely like to thank to Prof. Dr Mehmet Sağlam, Prof. Dr. Mithat Yüksel, Assoc. Prof. Dr. Levent Ballice, and Dr. Sezai Erdem for their superior supports and criticisms in preparation of this thesis.

I would like to thank to İsmail Hakkı Metecan, Ahmet Rasim Özkan, Rahim İşler, Hakan Madenoğlu, Tamer Karayıldırım and Murat Sert whom helped me a lot during my experiment.

I am also grateful to Ege Univesity Scientific Research Project Fund for their financial support.

And also I would like to thank to my family, especially my mother and my father for their support and patience.

# XI

## TABLE OF CONTENTS

|                                   | <b><u>Page</u></b> |
|-----------------------------------|--------------------|
| ÖZET                              | V                  |
| ABSTRACT                          | VII                |
| ACKNOWLEDGEMENT                   | IX                 |
| LIST OF FIGURES                   | XIX                |
| LIST OF TABLES                    | XXIX               |
| LIST OF SYMBOLS AND ABBREVIATIONS | XXXVIII            |
| 1. INTRODUCTION                   | 1                  |
| 2. GENERAL INFORMATION            | 4                  |
| 2.1 Definition of Sewage Sludge   | 4                  |

## **TABLE OF CONTENTS (continued)**

|       |                                                 | <b><u>Page</u></b> |
|-------|-------------------------------------------------|--------------------|
| 2.2   | Total Sludge Formation in World                 | 14                 |
| 2.3   | Total Sludge Formation in Turkey                | 15                 |
| 2.4   | Wastewater Treatment Processes                  | 19                 |
| 2.4.1 | Physical Unit Operations (Primary Treatment)    | 20                 |
| 2.4.2 | Chemical Unit Processes (Secondary Treatment)   | 21                 |
| 2.4.3 | Biological Unit Processes (Secondary Treatment) | 28                 |
| 2.5   | Petkim Wastewater Treatment Plant               | 30                 |
| 2.5.1 | Oily Wastewater Treatment Unit                  | 31                 |
| 2.5.2 | Sanitary Wastewater Treatment Unit              | 36                 |
| 2.5.3 | Chemical Wastewater Treatment Unit              | 37                 |
| 2.5.4 | Incineration Unit                               | 39                 |

## **TABLE OF CONTENTS (continued)**

|                                                     | <b><u>Page</u></b> |
|-----------------------------------------------------|--------------------|
| 2.6 Disposal Methods of Sewage Sludge               | 41                 |
| 2.7 Current Biomass Conversion Technologies         | 44                 |
| 2.7.1 Gasification of Biomass                       | 46                 |
| 2.7.1.1 Steam Reforming of Biomass                  | 47                 |
| 2.7.2 Pyrolysis of Biomass                          | 48                 |
| 2.7.3 Co-firing of Biomass and Coal Blends          | 50                 |
| 2.8 Supercritical Fluid Extraction of Sewage Sludge | 51                 |
| 2.9 Soxhlet Extraction                              | 53                 |
| 2.10 Liquid Absorption Chromatography               | 54                 |
| 3. LITERATURE REVIEW                                | 56                 |
| 4. MATERIAL AND METHOD                              | 63                 |

## TABLE OF CONTENTS (continued)

|         | <b><u>Page</u></b>                                                               |
|---------|----------------------------------------------------------------------------------|
| 4.1     | Material 63                                                                      |
| 4.1.1   | Sewage Sludge Produced from Petkim Wastewater Treatment Plant 63                 |
| 4.1.2   | Solvents 67                                                                      |
| 4.2     | Method 68                                                                        |
| 4.2.1   | Soxhlet Extraction of Sewage Sludge 68                                           |
| 4.2.2   | Supercritical Fluid Extraction of Sewage Sludge and<br>Experimental Procedure 69 |
| 4.2.3   | Analytical Methods 75                                                            |
| 4.2.3.1 | Gas Chromatography 75                                                            |
| 4.2.3.2 | Infrared Spectroscopy (IR) 77                                                    |
| 4.2.3.3 | Liquid Absorption Chromatography 77                                              |

## **TABLE OF CONTENTS (continued)**

|                                                                 | <b><u>Page</u></b> |
|-----------------------------------------------------------------|--------------------|
| <b>5. EVALUATION OF RESULTS</b>                                 | <b>86</b>          |
| 5.1 Soxhlet Extraction of Activated Sludge                      | 86                 |
| 5.2 Supercritical Fluid Extraction of Activated Sludge          | 88                 |
| 5.2.1 Effect of Solvent/Solid Ratio on Product Yield            | 89                 |
| 5.2.1.1 Supercritical Water Extraction                          | 89                 |
| 5.2.1.2 Supercritical Toluene Extraction                        | 93                 |
| 5.2.2 Effect of Temperature on Product Yield                    | 97                 |
| 5.2.2.1 Supercritical Water Extraction                          | 97                 |
| 5.2.2.2 Supercritical Toluene Extraction                        | 100                |
| 5.2.3 Effect of solvent/solid ratio on gas product distribution | 104                |
| 5.2.3.1 Supercritical Water Extraction                          | 104                |

## TABLE OF CONTENTS (continued)

|                                                            | <b><u>Page</u></b> |
|------------------------------------------------------------|--------------------|
| 5.2.3.2 Supercritical Toluene Extraction                   | 111                |
| 5.2.4 Effect of temperature on gas product distribution    | 117                |
| 5.2.4.1 Supercritical Water Extraction                     | 117                |
| 5.2.4.2 Supercritical Toluene Extraction                   | 127                |
| 5.2.5 Effect of temperature on liquid product distribution | 135                |
| 5.2.5.1 Supercritical Water Extraction                     | 135                |
| 5.2.5.2 Supercritical Toluene Extraction                   | 143                |
| 6. CONCLUSION                                              | 152                |
| REFERENCES                                                 | 159                |
| APPENDIX                                                   | 165                |
| RESUME                                                     | 169                |

## LIST OF FIGURES

### **Figure**

### **Page**

|      |                                                                                                                                                                                                                                                                                                                        |    |
|------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| 2.1  | Natural synthesis of humus                                                                                                                                                                                                                                                                                             | 8  |
| 2.2  | Proposed model for humic acid structure                                                                                                                                                                                                                                                                                | 9  |
| 2.3  | Formation of flocs                                                                                                                                                                                                                                                                                                     | 26 |
| 2.4  | Schematic actions of colloids and coagulation<br>(a) Forces acting on hydrophobic colloids in stable suspension.<br>(b) Compression of the double-layer charge on colloids (destabilization)<br>by addition of chemical coagulants.<br>(c) Agglomeration resulting from coagulation with metal salt and<br>polymer aid | 27 |
| 2.5  | Biological degradation of organic matters                                                                                                                                                                                                                                                                              | 30 |
| 2.6  | Petkim petrochemical complex wastewater treatment plant                                                                                                                                                                                                                                                                | 40 |
| 2.7  | Products from thermal biomass conversion                                                                                                                                                                                                                                                                               | 46 |
| 2.8  | Applications for bio-oil                                                                                                                                                                                                                                                                                               | 48 |
| 2.9  | Soxhlet extraction apparatus                                                                                                                                                                                                                                                                                           | 54 |
| 2.10 | The expected elution order of organic classes                                                                                                                                                                                                                                                                          | 55 |
| 4.1  | Schematic view of autoclave and its auxiliaries                                                                                                                                                                                                                                                                        | 69 |

## LIST OF FIGURES (continued)

| <b><u>Figure</u></b>                                                                                 | <b><u>Page</u></b> |
|------------------------------------------------------------------------------------------------------|--------------------|
| 4.2 Autoclave and its auxiliaries                                                                    | 70                 |
| 4.3 Introducing gaseous products into gas sampling bulb                                              | 71                 |
| 4.4 T-x-y diagrams for THF-water systems                                                             | 72                 |
| 4.5 Sequence of Experimental Procedures and Product Analysis                                         | 74                 |
| 4.6 Liquid Absorption Chromatography                                                                 | 78                 |
| 4.7 Gas chromatogram of aliphatic fraction of oil extracted with water<br>at 350°C (5-17.5 min.)     | 82                 |
| 4.8 Gas chromatogram of aliphatic fraction of oil extracted with water<br>at 350°C (17.5-30 min.)    | 83                 |
| 4.9 Gas chromatogram of aliphatic fraction of oil extracted with toluene<br>at 350°C (5-22.5 min.)   | 84                 |
| 4.10 Gas chromatogram of aliphatic fraction of oil extracted with toluene<br>at 350°C (22.5-40 min.) | 85                 |
| 5.1 Variation of SCWE product yield with solvent/solid ratio at 400°C                                | 91                 |
| 5.2 Variation of SCWE product yield with solvent/solid ratio at 425°C                                | 92                 |

## LIST OF FIGURES (continued)

### **Figure**

### **Page**

|      |                                                                                                          |     |
|------|----------------------------------------------------------------------------------------------------------|-----|
| 5.3  | Variation of SCTE product yield with solvent/solid ratio at 400°C                                        | 95  |
| 5.4  | Variation of SCTE product yield with solvent/solid ratio at 425°C                                        | 95  |
| 5.5  | Variation of SCWE product yieldwith temperature<br>(Solvent/Solid Ratio: 1)                              | 99  |
| 5.6  | Variation of SCWE total product yieldwith temperature<br>(Solvent/Solid Ratio: 1)                        | 100 |
| 5.7  | Variation of SCTE product yield with temperature<br>(Solvent/Solid Ratio: 1)                             | 102 |
| 5.8  | Variation of SCTE total productyield with temperature<br>(Solvent/Solid Ratio: 1)                        | 103 |
| 5.9  | Variation of total conversion of organic matter in SCWE and SCTE<br>of activated sludge with temperature | 103 |
| 5.10 | Variation of gas product distribution of SCWE at 400°C<br>(by volume percentage)                         | 106 |
| 5.11 | Variation of gas product distribution of SCWE at 400°C<br>(by weight percentage)                         | 107 |
| 5.12 | Variation of gas product distribution ofSCWE at 425°C<br>(by volume percentage)                          | 109 |

## LIST OF FIGURES (continued)

### **Figure**

### **Page**

|                                                                                                                         |     |
|-------------------------------------------------------------------------------------------------------------------------|-----|
| 5.13 Variation of gas product distribution of SCWE at 425°C<br>(by weight percentage)                                   | 110 |
| 5.14 Variation of gas product distribution of SCTE at 400°C<br>(by volume percentage)                                   | 112 |
| 5.15 Variation of gas product distribution of SCTE at 400°C<br>(by weight percentage)                                   | 113 |
| 5.16 Variation of gas product distribution of SCTE at 425°C<br>(by volume percentage)                                   | 115 |
| 5.17 Variation of gas product distribution of SCTE at 425°C<br>(by weight percentage)                                   | 116 |
| 5.18 Variation of gas product distribution of SCWEwith temperature<br>(Solvent/Solid Ratio: 1 and by volume percentage) | 120 |
| 5.19 Variation of gas product distribution of SCWEwith temperature<br>(Solvent/Solid Ratio: 1 and by volume of gas, mL) | 122 |
| 5.20 Variation of gas product distribution of SCWEwith temperature<br>(Solvent/Solid Ratio: 1 and by weight percentage) | 124 |
| 5.21 Variation of gas product distribution of SCWE with temperature<br>(Solvent/Solid Ratio: 1 and by weight of gas, g) | 126 |

## LIST OF FIGURES (continued)

### **Figure**

### **Page**

|                                                                                                                          |     |
|--------------------------------------------------------------------------------------------------------------------------|-----|
| 5.22 Variation of gas product distribution of SCTE with temperature<br>(Solvent/Solid Ratio: 1 and by volume percentage) | 128 |
| 5.23 Variation of gas product distribution of SCTE with temperature<br>(Solvent/Solid Ratio: 1 and by volume of gas, mL) | 130 |
| 5.24 Variation of gas product distribution of SCTE with temperature<br>(Solvent/Solid Ratio: 1 and by weight percentage) | 132 |
| 5.25 Variation of gas product distribution of SCTE with temperature<br>(Solvent/Solid Ratio: 1 and by weight of gas, g)  | 134 |
| 5.26 Variation of aliphatic fraction of SCWE oil                                                                         | 136 |
| 5.26 Simulated distillation curves of aliphatic fractions of oils obtained<br>from SCWE of activated sludge              | 137 |
| 5.28 IR spectrum of deasphalted oil extracted with water at 350°C                                                        | 139 |
| 5.29 IR spectrum of deasphalted oil extracted with water at 375°C                                                        | 140 |
| 5.30 IR spectrum of deasphalted oil extracted with water at 400°C                                                        | 141 |
| 5.31 IR spectrum of deasphalted oil extracted with water at 425°C                                                        | 142 |
| 5.32 Variation of aliphatic fraction of SCTE oil                                                                         | 144 |

## LIST OF FIGURES (continued)

### **Figure**

### **Page**

|      |                                                                                                     |     |
|------|-----------------------------------------------------------------------------------------------------|-----|
| 5.33 | Simulated distillation curves of aliphatic fractions of oils obtained from SCTE of activated sludge | 145 |
| 5.34 | IR spectrum of deasphalted oil extracted with toluene at 300°C                                      | 147 |
| 5.35 | IR spectrum of deasphalted oil extracted with toluene at 325°C                                      | 148 |
| 5.36 | IR spectrum of deasphalted oil extracted with toluene at 375°C                                      | 149 |
| 5.37 | IR spectrum of deasphalted oil extracted with toluene at 400°C                                      | 150 |
| 5.38 | IR spectrum of deasphalted oil extracted with toluene at 425°C                                      | 151 |

## LIST OF TABLES

| <b><u>Table</u></b>                                                                                                  | <b><u>Page</u></b> |
|----------------------------------------------------------------------------------------------------------------------|--------------------|
| 2.1 Types of sewage sludge                                                                                           | 5                  |
| 2.2 Physical characteristics of wastewater and their sources                                                         | 10                 |
| 2.3 Chemical characteristics of wastewater and their sources                                                         | 10                 |
| 2.4 Biological characteristics of wastewater and their sources                                                       | 12                 |
| 2.5 Important contaminants of concern in wastewater treatment                                                        | 12                 |
| 2.6 Sewage sludge generation rates                                                                                   | 14                 |
| 2.7 Fundamental environmental information of production industry waste inventory                                     | 16                 |
| 2.8 Total amount of sewage sludge produced in Turkey and number of plants according to disposal methods              | 17                 |
| 2.9 Total amount of sewage sludge produced in Turkey (by sectors) and number of plants according to disposal methods | 18                 |
| 2.10 Applications of physical unit operations in wastewater treatment                                                | 20                 |
| 2.11 Applications of chemical unit processes in wastewater treatment                                                 | 22                 |
| 2.12 Comparison of liquefaction and pyrolysis                                                                        | 49                 |
| 2.13 Temperature ranges for different compounds to decompose                                                         | 50                 |

## LIST OF TABLES (continued)

| <b><u>Table</u></b>                                                                                             | <b><u>Page</u></b> |
|-----------------------------------------------------------------------------------------------------------------|--------------------|
| 4.1 Effluent of flotation sludge centrifuge                                                                     | 64                 |
| 4.2 Effluent of biological sludge centrifuge                                                                    | 65                 |
| 4.3 Properties of dewatered sewage sludge                                                                       | 66                 |
| 4.4 Inorganic content and trace elements in sewage sludge (wt %)                                                | 67                 |
| 4.5 Operating conditions of gas chromatography for H <sub>2</sub> analysis                                      | 75                 |
| 4.6 Operating conditions of gas chromatography for CO <sub>2</sub> and C <sub>1</sub> -C <sub>6+</sub> analysis | 76                 |
| 4.7 Operating conditions of gas chromatography for CO analysis                                                  | 76                 |
| 4.8 Distillation fractions of petroleum hydrocarbons                                                            | 80                 |
| 4.9 Operating conditions of gas chromatography for analysis of aliphatic fractions                              | 81                 |
| 5.1 Soxhlet extraction of sewage sludge obtained from Aliaga-petrochemical complex wastewater treatment plant   | 87                 |
| 5.2 Operating conditions of activated sludge for SCWE                                                           | 90                 |
| 5.3 Variation product yield with solvent/solid ratio for SCWE at selected temperatures                          | 91                 |

## LIST OF TABLES (continued)

### **Table**

### **Page**

|      |                                                                                                                                           |     |
|------|-------------------------------------------------------------------------------------------------------------------------------------------|-----|
| 5.4  | Variation of total product yield and total conversion of organic matter (TCOM) with solvent/solid ratio for SCWE at selected temperatures | 92  |
| 5.5  | Operating conditions of activated sludge for SCTE                                                                                         | 93  |
| 5.6  | Variation of product yield with solvent/solid ratio for SCTE at selected temperatures                                                     | 94  |
| 5.7  | Variation of total product yield and total conversion of organic matter (TCOM) with solvent/solid ratio for SCTE at selected temperatures | 96  |
| 5.8  | Operating conditions of activated sludge for SCWE                                                                                         | 98  |
| 5.9  | Variation product yield with temperature for SCWE (Solvent/Solid Ratio: 1)                                                                | 99  |
| 5.10 | Operating conditions of activated sludge for SCTE                                                                                         | 101 |
| 5.11 | Variation of product yield with temperature for SCTE (Solvent/Solid Ratio: 1)                                                             | 101 |
| 5.12 | Variation of gas product distribution at 400°C for SCWE (by volume percentage)                                                            | 106 |
| 5.13 | Variation of gas product distribution at 400°C for SCWE (by weight percentage)                                                            | 107 |

## LIST OF TABLES (continued)

| <b><u>Table</u></b>                                                                                                       | <b><u>Page</u></b> |
|---------------------------------------------------------------------------------------------------------------------------|--------------------|
| 5.14 Variation of gas product distribution at 425°C for SCWE<br>(by volume percentage)                                    | 109                |
| 5.15 Variation of gas product distribution at 425°C for SCWE<br>(by weight percentage)                                    | 110                |
| 5.16 Variation of gas product distribution at 400°C for SCTE<br>(by volume percentage)                                    | 112                |
| 5.17 Variation of gas product distribution at 400°C for SCTE<br>(by weight percentage)                                    | 113                |
| 5.18 Variation of gas product distribution at 425°C for SCTE<br>(by volume percentage)                                    | 115                |
| 5.19 Variation of gas product distribution at 425°C for SCTE<br>(by weight percentage)                                    | 116                |
| 5.20 Variation of gas product distribution with temperature for SCWE<br>(Solvent/Solid Ratio: 1 and by volume percentage) | 119                |
| 5.21 Variation of gas product distribution with temperature for SCWE<br>(Solvent/Solid Ratio: 1 and by volume of gas, mL) | 121                |
| 5.22 Variation of gas product distribution with temperature for SCWE<br>(Solvent/Solid Ratio: 1 and by weight percentage) | 123                |

## LIST OF TABLES (continued)

| <b><u>Table</u></b>                                                                                                       | <b><u>Page</u></b> |
|---------------------------------------------------------------------------------------------------------------------------|--------------------|
| 5.23 Variation of gas product distribution with temperature for SCWE<br>(Solvent/Solid Ratio: 1 and by weight of gas, g)  | 125                |
| 5.24 Variation of gas product distribution with temperature for SCTE<br>(Solvent/Solid Ratio: 1 and by volume percentage) | 127                |
| 5.25 Variation of gas product distribution with temperature for SCTE<br>(Solvent/Solid Ratio: 1 and by volume of gas, mL) | 129                |
| 5.26 Variation of gas product distribution with temperature for SCWE<br>(Solvent/Solid Ratio: 1 and by weight percentage) | 131                |
| 5.27 Variation of gas product distribution with temperature for SCWE<br>(Solvent/Solid Ratio: 1 and by weight of gas, g)  | 133                |
| 5.28 Aliphatic fraction of oil for SCWE                                                                                   | 136                |
| 5.29 Aliphatic/Aromatic ratio of oil for SCWE                                                                             | 138                |
| 5.30 Aliphatic fraction of oil for SCTE                                                                                   | 143                |
| 5.31 Aliphatic/Aromatic ratio of oil for SCTE                                                                             | 146                |

## LIST OF SYMBOLS AND ABBREVIATIONS

| <b><u>Symbols</u></b>       | <b><u>Description</u></b>        |      |
|-----------------------------|----------------------------------|------|
| T                           | Temperature                      | (°C) |
|                             |                                  |      |
|                             |                                  |      |
|                             |                                  |      |
|                             |                                  |      |
|                             |                                  |      |
| <b><u>Abbreviations</u></b> |                                  |      |
| asp                         | Asphaltene                       |      |
| d                           | Dry                              |      |
| daf                         | Dry and ash free                 |      |
| h                           | Hour                             |      |
| min                         | Minute                           |      |
| mL                          | Milliliter                       |      |
| preasp                      | Preasphaltene                    |      |
| s                           | Second                           |      |
| SCF                         | Supercritical fluid              |      |
| SCFE                        | Supercritical fluid extraction   |      |
| SCT                         | Supercritical toluene            |      |
| SCTE                        | Supercritical toluene extraction |      |
| SCW                         | Supercritical water              |      |
| SCWE                        | Supercritical water extraction   |      |
| v                           | Volume                           |      |
| wt                          | Weight                           |      |

## 1. INTRODUCTION

Coal, petroleum and natural gas are the traditional fossil fuels whose direct use today accounts for most of the world's energy consumption. These resources are still being consumed rapidly. As the reserves of these energy sources are limited and diminish day by day, research on alternative energy sources are getting important. Especially, renewable energy sources like solar energy, nuclear energy and biomass attract interest of many researchers. Because, renewable energy is of growing importance in satisfying environmental concerns over fossil fuel usage. Sewage sludge and other forms of biomass including energy crops are some of the main renewable energy source available. These can provide the source of renewable liquid, gaseous and solid fuels. Biomass is considered the renewable energy source with the highest potential to contribute to the energy needs of modern society for both developed and developing economies world-wide.

Increasing industrialization and urbanization have resulted in a dramatic increase in the volume of wastewater produced around the world. Restrictions of environmental standards have meant that much of this wastewater has to be treated before it can be safely discharged. Each component of the sludge has its own environmental impact, which must be taken into account when choosing disposal route. The final resting place of the sludge must be either on the land, in the air or in the water after utilization with suitable methods. Disposal of sludge to land is widely used, but suitable sites are become less and controls on toxic materials like heavy metals, pathogens, toxic organics become more stringent. High temperature incineration or pyrolysis of sludge processes produce mainly CO<sub>2</sub> and inorganic material as a dry ash and provide large volume reduction. On the other hand, pyrolysis process produce liquid hydrocarbon which can be used as a diesel fuel. Another disposal method is dumping sludge to the ocean or sea, but is now to be banned because of its perceived environmental effects. Advantage and disadvantage of these disposal methods must be taken into consideration when deciding on the discarding of sludge.

In the two last decades, wastewater treatment has been a very important development probably due to the increasing limitations in water disposal. Due to this increase, the amount of sewage sludge also increased in accordance with this development. In the European Union,

the amount of sewage sludge is expected to increase by 50% at least 11.2 million tones dry solid by 2005. (Fullana et al., 2003)

According to inventory of waste of production industry in 1996 applied by statistical institute of state of Turkey, shows that 3.3 million tones of dry sewage sludge produced in the 476 wastewater treatment plants where 1000 million m<sup>3</sup> of wastewater discharged yearly. This survey also highlights the disposal methods of different manufacturing industries in Turkey. 40.69% of the sewage sludge was disposed by land applications (landfilling, burial etc.), 21.99% of the sewage sludge was dumped in municipal garbage and remaining amount were incinerated, dumped in sea and used in agricultural fields. (www.die.gov.tr)

Biomass fuels and residues can be converted to energy via thermal, biological and physical processes. Thermal processes are described with the greatest emphasis on the technologies that are attracting the most attention in the research, demonstration and commercial arenas.

There are many thermal processes available for converting biomass to a more useful energy form by combustion, gasification, pyrolysis and supercritical fluid extraction. There are many researches present on liquid fuel production from sewage sludge by pyrolysis process. But supercritical water (SCW) and supercritical toluene (SCT) extractions of sewage sludge were not encountered on literature. The primary purpose of this study was to identify environmental problems encountered and minimize these effects by converting petrochemical originated sewage sludge into valuable chemicals and energy sources by SCW and SCT extractions. Also, optimum reaction conditions such as type of solvent, reaction temperature and solvent/sludge ratio were examined to obtain maximum product yield. It is expected that these applications would have a high return in national economy by providing sludge to be converted into valuable energy and petroleum feedstock.

## 2. GENERAL INFORMATION

### 2.1 Definition of Sewage Sludge

Sewage sludge is a consolidate mixture of solids and water that emerge as a result of the physical, chemical and biological processes in wastewater treatment plant. Source of wastewater produced can be divided into two groups: industrial and municipal (also called as domestic or sanitary) wastewater. Industrial wastewater is produced during processing of goods, washing of equipments or goods and water used in boiler or cooler. Municipal wastewater includes products formed by daily activity of human beings. The nature of sewage sludge depends on the wastewater treatment process and on the source of the sewage. It can contain not only organic and inorganic matter, but also bacteria and virus, oil and grease, nutrients such as nitrogen phosphorus, heavy metals (As, Hg, Cd, Cr, Pb, Ni, Zn, Cu etc.) and organochlorines (PCBs, dieldrin, heptachlor etc.). (Weismantel, G. E., 1991)

Each type of sludge (Table 2.1) has different properties in relation to, for example, pumping, chemical conditioning and filtration. (Weismantel, G. E., 1991)

**Table 2.1:** Types of sewage sludge

| Sludge     | General Description                                                                                 |
|------------|-----------------------------------------------------------------------------------------------------|
| Primary    | Produced from primary settlement. Contains raw sewage solids.<br>Concentration:3-4%                 |
| Humus      | The excess biofilm from trickling filters. Typical concentrations: 2%                               |
| Activated  | Flocculated biomass produced in the activated sludge process.<br>Concentration (as wasted): 8-12g/L |
| Secondary  | Activated or humus                                                                                  |
| Co-settled | Mixture of primary and secondary solids produced in primary settlement tanks                        |
| Raw        | Untreated any way. Usually refers to primary or co-settled sludges                                  |

The particulates in water are broadly categorized into three major size groups: colloidal particles, with an upper limit of approximately  $1\text{ }\mu\text{m}$  and a lower limit of approximately  $0.5\text{ nm}$  and, suspended solids, consisting of particulates larger than approximately  $0.5\text{ }\mu\text{m}$ . Particulates smaller than  $5\text{ nm}$  are considered to be in true solution (dissolved substances).

Suspended solids may be mineral in origin (sand, silt, clays, etc.) or organic (products resulting from the decomposition of plant or animal matter, humic or fulvic acid, for example). Added to these compounds are microorganism such as bacteria, algae and viruses. Colloidal particles are suspended solids of the same origin. Dissolved substances are usually cations or anions. Part of the organic matter is also dissolved. Gases are also present ( $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ , etc.)

In addition to classification by size, colloidal and coarse particulate suspensions are also characterized according to the nature of their water-solid interface. Hydrophobic particulates have a well-defined interface between the water and solid phases and have a low affinity for water molecules. They are thermodynamically unstable and will aggregate irreversibly over time. Hydrophilic particulates are characterized by the lack of a clear phase boundary and are generally solutions of macromolecular organic compounds, such as protein and humic acids. The particulate suspensions can be reconstituted after aggregation and are thus reversible.

Hydrophobic particulates in water are primarily of an inorganic origin and include some clay particulates and non-hydrated metal oxides. Many inorganic particulates in natural waters show some hydrophilic properties because water molecules will bind to the surface. Examples include hydrated metal oxides (iron or aluminum oxides) and silica ( $\text{SiO}_2$ ) and asbestos fiber.

In contrast to hydrophobic particulates, hydrophilic particulates are primarily of organic origin and include a wide diversity of biocolloids (humic and fulvic acids, viruses) and suspended living or dead microorganisms (bacteria, algae). Because biocolloids may adsorb on the surfaces of inorganic particulates, particulates generally exhibit heterogeneous surface properties in natural water systems. Organic compounds in water derive from natural decomposition of plant and animal material; from industrial, urban and agricultural pollution, and from the reaction of halides (most often chlorine) with natural organics during water treatment.



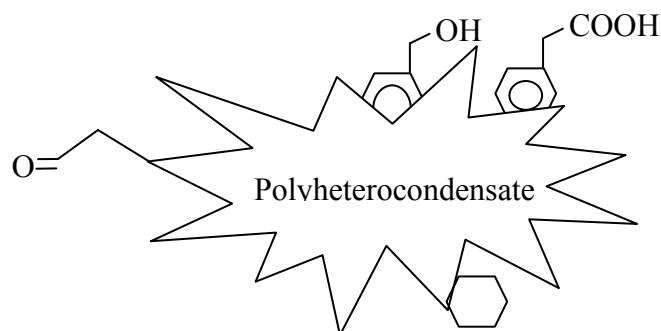


**Figure 2.2:** Proposed model for humic acid structure

Physical, chemical and biological characteristics of wastewater and their sources are given in Table 2.2, 2.3 and 2.4. Also, important contaminants of concern in wastewater treatment are tabulated in Table 2.5. (Metcalf and Eddy, 1991)

**Table 2.2:** Physical characteristics of wastewater and their sources

| Characteristics                    | Sources                                                                                  |
|------------------------------------|------------------------------------------------------------------------------------------|
| <b><u>Physical properties:</u></b> |                                                                                          |
| Color                              | Domestic and industrial wastes, natural decay of organic materials                       |
| Odor                               | Decomposing water supply, domestic and industrial wastes                                 |
| Solids                             | Domestic water supply, Domestic and industrial wastes, soil erosion, inflow/infiltration |
| Temperature                        | Domestic and industrial wastes                                                           |

**Table 2.3:** Chemical characteristics of wastewater and their sources

| Characteristics                      | Sources                                                           |
|--------------------------------------|-------------------------------------------------------------------|
| <b><u>Chemical constituents:</u></b> |                                                                   |
| <b>Organic:</b>                      |                                                                   |
| Carbohydrates                        | Domestic, commercial and industrial wastes                        |
| Fats, oils and greases               | Domestic, commercial and industrial wastes                        |
| Pesticides                           | Agricultural wastes                                               |
| Phenol                               | Industrial wastes                                                 |
| Proteins                             | Domestic, commercial and industrial wastes                        |
| Priority pollutants                  | Domestic, commercial and industrial wastes                        |
| Surfactants                          | Domestic, commercial and industrial wastes                        |
| Volatile organic compounds           | Domestic, commercial and industrial wastes                        |
| Other                                | Natural decay of organic materials                                |
| <b>Inorganic:</b>                    |                                                                   |
| Alkalinity                           | Domestic wastes, domestic water supply, groundwater infiltration  |
| Chlorides                            | Domestic wastes, domestic water supply, groundwater infiltration  |
| Heavy metals                         | Industrial wastes                                                 |
| Nitrogen                             | Domestic and agricultural wastes                                  |
| pH                                   | Domestic, commercial and industrial wastes                        |
| Phosphorus                           | Domestic, commercial and industrial wastes; natural runoff        |
| Priority pollutants                  | Domestic, commercial and industrial wastes                        |
| Sulfur                               | Domestic water supply; domestic, commercial and industrial wastes |
| <b>Gases:</b>                        |                                                                   |
| Hydrogen sulfide                     | Decomposition of domestic wastes                                  |
| Methane                              | Decomposition of domestic wastes                                  |
| Oxygen                               | Domestic water supply, surface water filtration                   |

**Table 2.4:** Biological characteristics of wastewater and their sources

| Characteristics                        | Sources                                                       |
|----------------------------------------|---------------------------------------------------------------|
| <b><u>Biological constituents:</u></b> |                                                               |
| Animals                                | Open watercourses and treatment plants                        |
| Plants                                 | Open watercourses and treatment plants                        |
| <b>Protists:</b>                       |                                                               |
| Eubacteria                             | Domestic wastes, surface-water infiltration, treatment plants |
| Archaeobacteria                        | Domestic wastes, surface-water infiltration                   |

**Table 2.5:** Important contaminants of concern in wastewater treatment

| Contaminant            | Reason for importance                                                                                                                                                                                                                                                                                                     |
|------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Suspended solids       | Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharged in the aquatic environment.                                                                                                                                                              |
| Biodegradable organics | Composed principally of proteins, carbohydrates and fats, biodegradable organics are measured most commonly in terms of BOD* and COD**. If discharged untreated to the environment, their biological stabilization can lead to depletion of natural O <sub>2</sub> resources and to the development of septic conditions. |
| Pathogens              | Communicable diseases can be transmitted by the pathogenic organisms in wastewater.                                                                                                                                                                                                                                       |
| Nutrients              | Both nitrogen and phosphorus, along with carbon, are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the undesirable aquatic life. When discharged in excessive amounts on land, they can also lead to the pollution of groundwater.                              |

Table 2.5 continued

|                      |                                                                                                                                                                                                          |
|----------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Priority pollutants  | Organic and inorganic compounds selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity or high acute toxicity. Many of these compounds are found in wastewater. |
| Refractory Organics  | These organics tend to resist conventional methods of wastewater treatment. Typical examples include surfactants, phenols and agricultural pesticides.                                                   |
| Heavy Metals         | Heavy metals are usually added to wastewater from commercial and industrial activities and may have to be removed if the wastewater is to be reused.                                                     |
| Dissolved Inorganics | Inorganic constituents such as calcium, sodium and sulfate are added to the original domestic water supply as a result of use and may have to be removed if the wastewater is to be reused.              |

## 2.2 Total Sludge Formation in World

Conventional physico-chemical treatment of sewage or waste water will produce significant quantities of residual solids. The quantities of solid waste resulting from the treatment of sewage are given in Table 2.6 (EPA, Biosolids Generation, 1999). Large amounts of sewage sludge are generated annually in the United States and Western Europe.

Table 2.6: Sewage sludge generation rates

| Country | Amount (million tons dry solids/yr) | Disposal Method (%) |              |              |       |
|---------|-------------------------------------|---------------------|--------------|--------------|-------|
|         |                                     | Application to land | Land-filling | Incineration | Other |
| Austria | 320                                 | 13                  | 56           | 31           | 0     |
| Belgium | 75                                  | 31                  | 56           | 9            | 4     |
| Denmark | 130                                 | 37                  | 33           | 28           | 2     |
| France  | 700                                 | 50                  | 50           | 0            | 0     |
| Germany | 2500                                | 25                  | 63           | 12           | 0     |
| Greece  | 15                                  | 3                   | 97           | 0            | 0     |
| Italy   | 800                                 | 34                  | 55           | 11           | 0     |

Table 2.6 continued

|             |      |    |    |    |    |
|-------------|------|----|----|----|----|
| Spain       | 280  | 10 | 50 | 10 | 30 |
| Switzerland | 215  | 50 | 30 | 20 | 0  |
| U.K.        | 1107 | 55 | 8  | 7  | 30 |
| U. S. A     | 6900 | 41 | 17 | 22 | 20 |

### 2.3 Total Sludge Formation in Turkey

Production industry waste inventory research in 1996 has been applied to 2209 factory where 25 and more person is employed. Information are compiled related with water provided in respect of its sources, amount of water consumed, amount of wastewater, type of wastewater treatment plants and their capacities, amount of sewage sludge produced in treatment plants, quantity of industrial solid waste and its disposal, in the extent of production industry research in Turkey (Table 2.7). ([www.die.gov.tr](http://www.die.gov.tr))

According to report of statistical institute of state (in the scope of environmental statistics of solid wastes in the year of 1996) 3.2 million tones of sewage sludge are being generated annually from wastewater treatment facilities in Turkey. 40.69% of this sewage sludge is disposed of by landfilling, 21.99% is disposed to municipal garbage, 6.10% is used in agriculture, 4.66% is dumped in sea and 19.56% is discarded with other methods (incineration, burying and disposal to river or lake). Total amount of sludge produced and disposal methods according to some selected sectors are outlined in Table 2.8 and 2.9. ([www.die.gov.tr](http://www.die.gov.tr))

Classification of industries with International standards was done (31: food, drink and tobacco industry; 35: Chemistry-petroleum, coal, rubber and plastic products industry) (Table 2.9)

**Table 2.7:** Fundamental environmental information of production industry waste inventory

|                                                                                       |      |
|---------------------------------------------------------------------------------------|------|
| <b>Number of factory included in public survey</b>                                    | 2209 |
| <b>Number of factory that has wastewater treatment facilities</b>                     | 645  |
| <b>Number of factory that has at least one of the wastewater treatment facilities</b> | 616  |
| Number of factory that has only industrial wastewater treatment facilities            | 429  |

*Table 2.7 continued*

|                                                                              |      |
|------------------------------------------------------------------------------|------|
| Number of factory that has only municipal wastewater treatment facilities    | 92   |
| Number of factory that has both of the wastewater treatment facilities       | 95   |
| <b>Permission status of factory</b>                                          |      |
| Number of factory that has permission of wastewater discharge                | 396  |
| <b>Amount of water and wastewater of factory million m<sup>3</sup>/year)</b> |      |
| Water provided                                                               | 1820 |
| Water consumed                                                               | 1801 |
| Water recycled                                                               | 395  |
| Water discharged                                                             | 1000 |
| Industrial                                                                   | 911  |
| Municipal                                                                    | 89   |
| <b>Amount of solid waste of factory (million ton/year)</b>                   |      |
| Recovered                                                                    | 2.14 |
| Sold and donated                                                             | 7.10 |
| Disposed                                                                     | 8.77 |

17

**Table 2.8:** Total amount of sewage sludge produced in Turkey and number of plants according to disposal methods

| Class  | Sector | # of Plants | Amount of Sludge<br>(Tons/year) | Disposal Methods          |                    |                     |                                         |                                    |                     |                |
|--------|--------|-------------|---------------------------------|---------------------------|--------------------|---------------------|-----------------------------------------|------------------------------------|---------------------|----------------|
|        |        |             |                                 | Agricultural<br>Usage (%) | Sea Dumping<br>(%) | Land-Filling<br>(%) | Disposal to<br>Municipal<br>Garbage (%) | Disposal<br>to river or<br>lake(%) | Incineration<br>(%) | Burying<br>(%) |
| Turkey | A      | 476         | 3265441                         | 6.10                      | 4.66               | 40.69               | 21.99                                   | 0.52                               | 3.93                | 1.67           |
|        | B      | 61          | 2176700                         | 6.30                      | 6.91               | 55.25               | 13.44                                   | 0.78                               | 0.64                | 1.49           |
|        | C      | 415         | 1088741                         | 5.69                      | 0.15               | 11.57               | 39.09                                   | -                                  | 10.52               | 2.04           |

Sectors: A. Total B. State C. Private

**Table 2.9:** Total amount of sewage sludge produced in Turkey (by sectors) and number of plants according to disposal methods

| Class | Sector | # of Plants | Amount of Sludge<br>(Tons/year) | Disposal Methods          |                    |                     |                                         |                                    |                     |                |
|-------|--------|-------------|---------------------------------|---------------------------|--------------------|---------------------|-----------------------------------------|------------------------------------|---------------------|----------------|
|       |        |             |                                 | Agricultural<br>Usage (%) | Sea Dumping<br>(%) | Land-Filling<br>(%) | Disposal to<br>Municipal<br>Garbage (%) | Disposal<br>to river or<br>lake(%) | Incineration<br>(%) | Burying<br>(%) |
| 31    | A      | 108         | 2014027                         | 9.87                      | 7.45               | 37.30               | 22.38                                   | 0.84                               | -                   | -              |
|       | B      | 25          | 1442788                         | 9.50                      | 10.40              | 44.88               | 19.16                                   | 1.18                               | -                   | -              |
|       | C      | 83          | 571239                          | 10.78                     | -                  | 18.16               | 30.50                                   | -                                  | -                   | 0.01           |
| 35    | A      | 76          | 166809                          | 0.02                      | 0.28               | 6.43                | 6.79                                    | -                                  | 74.12               | 12.01          |
|       | B      | 11          | 45013                           | -                         | 1.03               | 23.13               | -                                       | -                                  | 30.99               | 44.44          |
|       | C      | 65          | 121796                          | 0.02                      | -                  | 0.26                | 9.3                                     | -                                  | 90.06               | 0.02           |

## **2.4 Wastewater Treatment Processes**

From the stand point of sources of generation, wastewater may be defined as a combination of the liquid- or water-carried wastes removed from residences, institutions, and commercial and industrial establishments, together with such groundwater, surface water, and stormwater as may be present.

The contaminants in wastewater are removed by physical, chemical, and biological means. The individual methods usually are classified as physical unit operations, chemical unit processes, and biological unit processes. Although these operations and processes occur in a variety of combinations in treatment systems, it has been found advantageous to understand their specific basis separately because the principles involved do not change.

Wastewater treatment has three stages: primary, secondary and tertiary.

- \*Primary – removes solid matter

- \*Secondary – removes dissolved organic matter

- \*Tertiary – disinfects (sometimes also removes inorganic nutrients)

Also, activated sludge and anaerobic digesters are the major methods. Both are microbial processes.

### **2.4.1 Physical Unit Operations (Primary Treatment)**

Treatment methods in which the application of physical forces predominates are known as physical unit operations. (Table 2.10) They were first to be used for wastewater treatment. Screening, mixing, sedimentation, flotation, flocculation, filtration, and gas transfer are typical unit operations. (Metcalf and Eddy, 1991)

**Table 2.10:** Applications of physical unit operations in wastewater treatment

| <b>Operation</b>                 | <b>Application</b>                                                                                                              |
|----------------------------------|---------------------------------------------------------------------------------------------------------------------------------|
| Flowmetering                     | Process control, process monitoring, and discharge reports                                                                      |
| Screening                        | Removal of coarse and settleable solids by interception (surface stripping)                                                     |
| Comminution                      | Grinding of coarse solids to a more or less uniform size                                                                        |
| Flow equalization                | Equalization of flow and mass loadings of BOD and suspended solids                                                              |
| Mixing                           | Mixing chemicals and gases with wastewater, and maintaining solids in suspension                                                |
| Flocculation                     | Promotes aggregation of small particles into larger particles to enhance their removal by gravity sedimentation                 |
| Sedimentation                    | Removal of settleable solids and thickening of sludges                                                                          |
| Flotation                        | Removal of fine residual suspended solids and particles with densities close to that of water. Also thickens biological sludges |
| Filtration                       | Removal of fine residual suspended solids remaining after biological or chemical treatment                                      |
| Microscreening                   | Same as filtration. Also removal of algae from stabilization-pond effluent                                                      |
| Gas transfer                     | Addition and removal of gases                                                                                                   |
| Volatilization and gas stripping | Emission of volatile and semi-volatile organic compounds from wastewaters                                                       |

### 2.4.2 Chemical Unit Processes (Secondary Treatment)

Treatment methods in which the removal or conversion of contaminants is brought about by the addition of chemicals or by other chemical reactions are known as chemical unit processes. (Table 2.11) Precipitation, coagulation, adsorption and disinfection are the most common examples used in wastewater treatment. (Metcalf and Eddy, 1991)

**Table 2.11:** Applications of chemical unit processes in wastewater treatment

| Process                              | Application                                                                                                                                                                       |
|--------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Chemical precipitation (coagulation) | Removal phosphorus and enhancement of suspended solids removal in primary sedimentation facilities used for physical-chemical treatment                                           |
| Adsorption                           | Removal of organics not removed by conventional chemical and biological treatment methods. Also used for dechlorination of wastewater before final discharge for treated effluent |
| Disinfection                         | Selective destruction of disease-causing organisms                                                                                                                                |
| Disinfection with chlorine           | Selective destruction of disease-causing organisms                                                                                                                                |
| Dechlorination                       | Selective destruction of disease-causing organisms                                                                                                                                |
| Disinfection with chlorine dioxide   | Selective destruction of disease-causing organisms                                                                                                                                |
| Disinfection with bromine chloride   | Selective destruction of disease-causing organisms                                                                                                                                |
| Disinfection with ozone              | Selective destruction of disease-causing organisms                                                                                                                                |
| Disinfection with ultraviolet light  | Selective destruction of disease-causing organisms                                                                                                                                |
| Other chemical applications          | Various other chemicals can be used to achieve specific objectives in wastewater treatment                                                                                        |

A large variety of turbidity-producing substances found in polluted waters do not settle out of solution, for example, color compounds, clay particles, microscopic organisms, and organic matter from decaying vegetation or municipal wastes. A colloidal dispersion formed by these particles is stable in quiescent water, since the individual particles have such a large

surface area relative to their weight that gravity forces do not influence their suspension. Colloids are classified as hydrophobic (water hating) and hydrophilic (water loving).

Hydrophilic colloids are stable because of their attraction for water molecules, rather than because of the slight charge that they might possess. Because of their affinity for water, they are not as easy to remove from suspension as hydrophobic colloids, and coagulant dosages of 10 to 20 times the amount used in conventional water treatment are frequently necessary to coagulate hydrophilic materials.

Hydrophobic particles, possessing no affinity for water, depend on electrical charge for their stability in suspension. The bulk of inorganic and organic matter in turbid natural water is of this type. In raw water, colloids invariably carry a negative charge (imperfection in crystalline structure, ionization of peripheral chemical groups, etc.). The forces acting on hydrophobic colloids are illustrated in Figure 2.4- a. Individual particles are held apart by electrostatic repulsion forces developed by positive ions adsorbed onto their surfaces from solution. An analogy is the repulsive force that exists between the common poles of two bar magnets. The magnitude of repulsive force developed by the charged double layer of ions attracted to a particle is referred to as the zeta potential.

A natural force of attraction exists between any two masses (Van der Waals Forces). Random motion of colloids, caused by bombardment of water molecules tends to enhance this physical force of attraction in pulling the particles together. However, a colloidal suspension remains dispersed indefinitely when the forces of repulsion exceed those of attraction and the particles are not allowed to contact.

The purpose of chemical coagulation in water treatment is to destabilize suspended contaminants such that the particles contract and agglomerate, forming flocs that drop out of solution by sedimentation. Destabilization of hydrophobic colloids is accomplished by addition of chemical coagulants, for instance, salts of aluminum and iron. Highly charged hydrolyzed metal ions produced by these salts in solution reduce the repulsive forces between colloids by compressing the diffuse double layer surrounding individual particles (Figure 2.4- b). With the forces of repulsion suppressed, gentle mixing results in particle contact, and the

force of attraction cause particles to stick to each other, producing progressive agglomeration. Coagulant aids may be used to enhance the process of flocculation. For example, organic polymers provide bridging between particles by attaching themselves to the absorbent surfaces of colloids, building larger flocculated masses (Figure 2.4- c). (Hammer, M. J., 1996)

Removal of turbidity by coagulation depends on the type of colloids in suspension,; the temperature, pH, and chemical composition of the water; the type and dosage of coagulants and aids; and degree and time of mixing provided for chemical dispersion and floc formation.

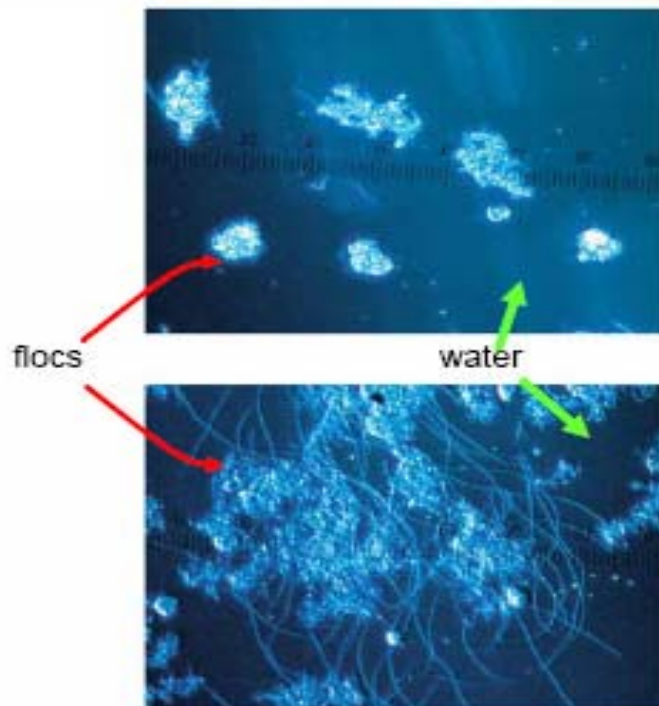


**Figure 2.3:** Formation of flocs

Coagulation and flocculation are associated with the processes used in chemical treatment. Mixing, involving violent agitation is used to dissolve and disperse coagulant chemicals throughout the water being treated. Flocculation is a slow mixing process, following chemical dispersion, during which the destabilized particles form into well-developed flocs of sufficient size to settle. The word coagulation is commonly used to describe the entire mixing and flocculation operation. Actual units used in chemical treatment may be constructed in series (mixing-flocculation-sedimentation) or may be housed in a single compartmented tank. (Hammer, M. J., 1996)

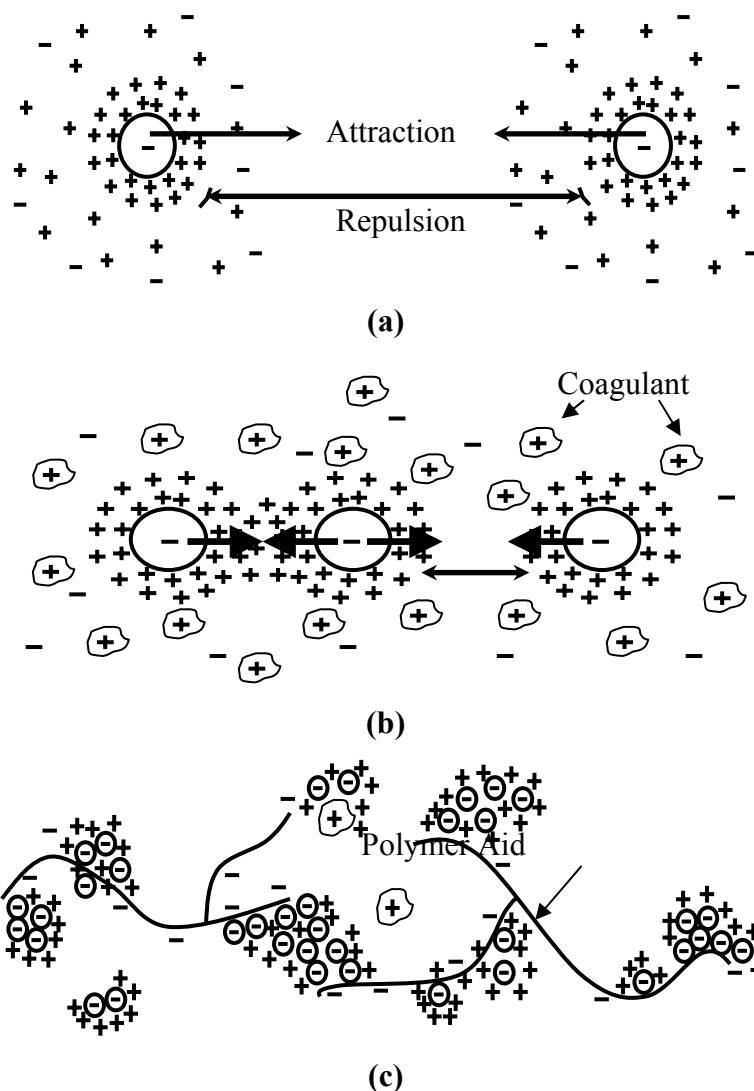


**Figure 2.4:** Schematic actions of colloids and coagulation. **(a)** Forces acting on hydrophobic colloids in stable suspension. **(b)** Compression of the double-layer charge on colloids (destabilization) by addition of chemical coagulants. **(c)** Agglomeration resulting from coagulation with metal salt and polymer aid.

### 2.4.3 Biological Unit Processes (Secondary Treatment)

Treatment methods in which the removal of contaminants is brought about by biological activity are known as biological unit processes. Biological treatment is used primarily to remove the biodegradable organic substances (colloidal or dissolved) in wastewater. Basically, these substances are converted into gases and into biological cell tissue that can be removed

by settling. Biological treatment is also used to remove nutrients (nitrogen and phosphorus) in wastewater.

Biodegradable organic matter in wastewater is classified into three major categories; carbohydrates, proteins, and fats. Carbohydrates consist of sugar units containing the elements of carbon, hydrogen, and oxygen. Polysaccharides, long chains of sugar units, can be divided into two groups: readily degradable starches abundant in potatoes, rice, corn, and other edible plants; and cellulose found in wood, cotton, paper, and similar plant tissues. Cellulose compounds degrade biologically at a much slower rate than starches. Proteins in the simple form are long strings of amino acids containing carbon, hydrogen, oxygen, nitrogen, and phosphorus. They form an essential part of all living tissue, and constitute a diet necessity for all higher animals. Fats refer to a variety of biochemical substances that have the common property of being soluble to varying degrees in organic solvents while being only soluble in water. Because of their limited solubility, degradation by microorganisms is at a very slow rate.

The majority of carbohydrates, proteins and fats in wastewater are in the form of large molecules that cannot penetrate the cell membrane of microorganisms. Bacteria, in order to metabolize high-molecular-weight substances, must be capable of breaking down the large molecules into diffusible fractions for assimilation into the cell. The first step in bacterial decomposition of organic compounds is hydrolysis of carbohydrates into soluble sugars, proteins into amino acids, and fats to short fatty acids. Further aerobic biodegradation results in the formation of carbon dioxide and water. By anaerobic digestion, decomposition in the absence of oxygen, the end products are organic acids, alcohols, and other liquid intermediates as well as gaseous entities of carbon dioxide, methane and hydrogen sulfide. 60 to 80 percent of the organic matter in wastewater is readily available for biodegradation. Petroleum derivatives, detergents, pesticides, and other synthetic organic compounds are resistant to biodegradation, and some are toxic and inhibit the activity of microorganisms in biological treatment processes. Biological degradation pathway of organic matters was given in Figure 2.5.

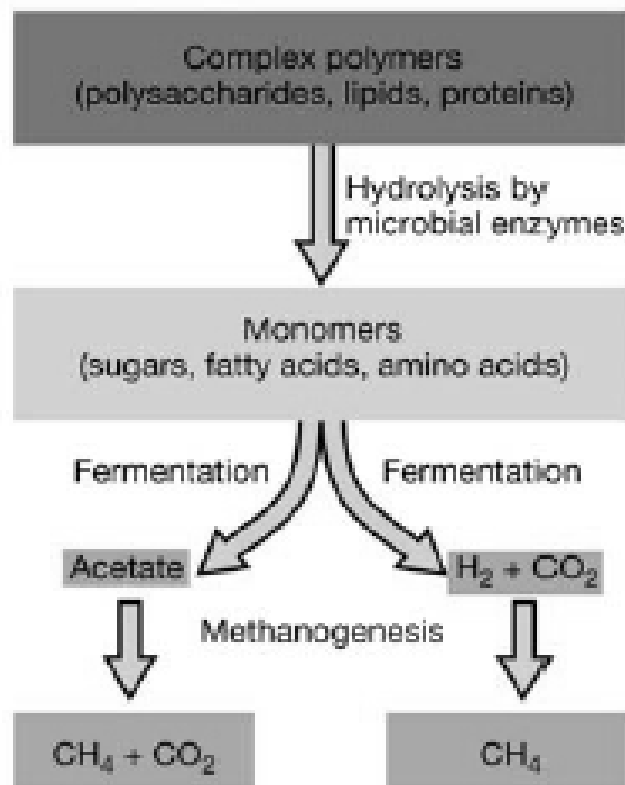


**Figure 2.5:** Biological degradation of organic matters

## 2.5 Petkim Wastewater Treatment Plant

Industrial wastes have an important effect on the environmental pollution. A petrochemical complex consists of different production plants and every unit may produce wastewater in different chemical composition. Wastewater treatment plant is designed to handle effluents and incineration of residue from complex wastewater. Generally, petrochemical wastes have high BOD (Biological Oxygen Demand, quantity of oxygen consumed at 20°C and in darkness during a given period to produce biological means oxidation of the biodegradable organic matter present in water) load and a great amount of organic materials. The main effluents, which originated in Aliğa Petrochemical Complex, are: Oily wastewater (550 m<sup>3</sup>/h), Sanitary wastewater (120 m<sup>3</sup>/h) and Chemical wastewater (1000 m<sup>3</sup>/h). (www.petkim.gov.tr)

### 2.5.1 Oily wastewater treatment unit

Effluent of the oily water system arrives to the base of the Archimedean screw pumps through two interceptors, and then to the large bar screen. The screen is design to retain the larger sized wastes in the effluent. All the effluent is pumped into the flow meter conduit where the flowmeter is installed. The water then flows into the A.P.I. Separators. If the level of the effluent in the screw pumps basin raises too high, a part of the water overflows into Holding Basin. The influent will be treated when the overflow decreases.

- **A.P.I. Separators**

An A.P.I. separator receives oily water from the Archimedean Screws and removes the oil and settled solids by means of gravity separation. Floating oil is directed toward the A.P.I. pipes by means of wings which extent across the width of the channel and move cyclically along the channel floor and the surface of the liquid. Skimmed oil, which contains a large percentage (80%) of water, is collected in a skimmed oil pit and transferred to the slop-oil tank. Bottom sludge withdrawal system consist sludge suction pipe located at the bottom of the sludge hopper. Bottom sludge is send to sludge pump and then transferred to thickeners. Separator effluents flow to flash mixing by gravity.

- **Coagulation-Flocculation**

Water undergoes chemical treatment in this tank, which has two compartments. The first compartment is equipped with a fast mixer and a pH probe. The influent is mixed with the following reagents;

-Aluminum sulphate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) for coagulation (Its dosage depends upon the flow rate of the influent to be treated)

-NaOH and  $\text{H}_2\text{SO}_4$  for neutralization (Their dosage depends upon the measured pH)

The influent flows under a baffle from the first compartment into the second compartment. Polyelectrolyte is added in this compartment that is equipped with a variable slow speed agitator to obtain good flocculation. Flocculated water flows over a weir into the distribution channel to the two flotators.

- **Flotation**

Influent enters through the intake pipe and passes into flotation chambers together with the pressurized water, which is saturated with air. The pressure on the water suddenly reduces to atmospheric pressure when it enters the tank and liberates micron-sized air bubbles, which attach themselves to the particles in suspension. Then, these rises to the surface of the liquid and floated scum is scraped into a sump. Bottom sludge is also scraped and sent to the sump. Floating and bottom sludge then pumped to the dewatering unit (flotation sludge centrifuge).

- **Aeration Basin (Biological Treatment Unit)**

This basin in which the biological treatment takes place is designed to receive the following;

- Treated effluent (Chemical-Physical) from the flotators.
- Influent sewer water from the factory and village interceptor after undergoing pre-treatment.

This basin has two parallel compartments and influent undergoes aerobic action of microorganisms, which oxidize large part of the dissolved matter contained in the effluent. The oxygen needed (0.5 to 2 mg/L) for this process is supplied by turbine type aerators which create turbulence and maintains the homogeneity of the activated sludge in the basin. The overflow from the aeration basin flows into a conduit, which leads to the clarifier (Settling basin). Since the concentration of the activated sludge in the aeration basin must be kept constant (3 mg/l), part of the sludge must be returned from the basin to settling basin. The decanted activated sludge from the settling basin makes up a part of the “return sludge”, but for the other part the aeration basin must be flushed of excess sludge to counter balance to increase in the mass of activated sludge due to the assimilation of the pollution. Biological treatment will be most effective if nitrogen and phosphorus content are maintained constant with respect to the pollution to be treated. Ammonia and phosphoric acid can be introduced to aeration basin intake in order to boost nitrogen and/or phosphorus deficiency.

- **Settling Basin**

Settling basin receives the mixed liquid from the aeration basin. Activated sludge is decanted and settles to the bottom of the tank. Biologically treated water flows into a

collection conduit which feeds into the treated water pit and which allows the treated water to flow by gravity into the final basin. Pumps are installed in treated water pit which conduct treated water into incinerator scrubber as cooling water. Siphoning action through piping attached to the rotating walkway, draws up activated sludge from the bottom of the tank and it is removed from the center of the tank. Sludge flows through pump into the pump basin (sludge pit). Excess sludge is withdrawn to the sludge treatment unit (Thickener) and some of sludge is returned to aeration basin.

- **Sludge Thickener**

Input to the sludge thickener is as follows;

- Excess biological sludge is fed directly into the tank by pumps.
- Sludge from A.P.I. separators, and which has been de-gritted in the hydrocyclone.

The thickener is equipped with a bottom scraper-scum breaker vertical paddle system for enhancing the thickness of the sludge. The sludge is then collected in a well at the bottom of the tank where it is extracted for dewatering by centrifuges. The overflow from the thickener returns to the head of the station (holding basin). The walkway bridge supporting the scraper-scum breaker mechanism also operates a surface scraper for removing any floating material into the hopper. This floating matter is extracted by pump and sent back to the slop oil pit, which is linked to the A.P.I. separators.

- **Sludge Dewatering**

Biological sludge centrifuge and flotation sludge centrifuge are used to decrease the water content of the sludge. The mechanical sludge dewatering unit is basically comprised of centrifuges. Dewatering takes place after having treated the sludge with coagulants. The following sludge is treated;

- Sludge from the thickener; that is biological sludge and sludge from the A.P.I. separators.
- Sludge from the flotators.

Sludge, in which appropriate amount of coagulant has been injected, is fed into the centrifuges where a separation takes place between the solids (sludge cake) and the liquid discharge. The liquid discharge is sent to the head of the station for treatment with the influent. Sludge cake drop into a feed hopper for the pump, which feeds the cake to the incinerators.

### 2.5.2 Sanitary Wastewater Treatment Unit

- **Pumping Station**

Wastewater is collected and pumped into treatment units.

- **Pretreatment Unit**

Particulates in wastewater are separated and pumped into biological treatment unit.

- **Aeration Basin (Biological Treatment Unit)**

Same aeration basin is used with oily wastewater treatment unit.

- **Settling Basin**

Same settling basin is used with oily wastewater treatment unit.

- **Sludge Thickener**

Same sludge thickener unit is used with oily wastewater treatment unit.

- **Sludge Dewatering**

Biological sludge centrifuge operates to decrease the water content of the sludge.

### 2.5.3 Chemical Wastewater Treatment Unit

- **Neutralization Basin**

Influent from the chemical wastewater unit arrives to neutralization basin for pH adjustment by an open channel. Neutralization achieved by adding NaOH and/or H<sub>2</sub>SO<sub>4</sub>.

- **Coagulation-Flocculation**

After pH adjustment, water flows to flash mixing and flocculation basins, for coagulation and flocculation. Aluminum sulphate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) and polyelectrolyte are supplied in this treatment processes.

- **Plate Type Separators**

After coagulation and flocculation treated water flows through the separators. Plates type separators are using for separating the phases. Settled sludge is removed by trac-vac system that is driving pneumatically under water. Collected sludge is discharged to thickener. Decanted water flows to upside between plates and discharged into the collection channels.

- **Settling Basin**

Water from the separators flows to settling basin and after than to final basin with treated oily and sanitary waters.

- **Sludge Thickener**

Chemical wastewater thickener unit operates to separate bottom sludge and floating materials.

- **Sludge Dewatering**

Chemical sludge centrifuge is used to decrease the water content of the sludge.

#### **2.5.4 Incineration Unit**

A fluidized bed incinerator is a vertical, cylindrical shaped furnace, which consists of three areas. The lower part of the reactor is called wind-box. Immediately above this is the fluidized bed. The highest area is called freeboard where solids and fluidization gas separation occurs. Fluidization consists of placing the solid particles in suspension in a sand bed with

forced air from blowers; solid-gas mixture has characteristics of fluid. The fluidized bed creates an ideal medium for thermal oxidation of most of the wastes. The water content is evaporated and the combustible solids, liquids and vapors react with oxygen in the fluidized airflow. Complete combustion is accompanied by supplying minimum amount of excess air (40%) and minimum reaction temperature is obtained due to turbulence of fluidized bed.

Another advantage of fluidization is that it acts as a heat source, which ensures uniform temperature (720-750°C) and a constant reaction. The exhaust gases containing the mineral parts of the waste in the form of very fine particles, are cooled in a cooling tower (quench), and then passed through a venture scrubber and are discharged into the atmosphere. The ash water is drained into a lagoon (ash basin) where ash decanted by gravity while the water passed over a weir to flow into the final basin. Lower heating values of volatile matter and oily matter are 5500 kcal/kg and 9000 kcal/kg, respectively.

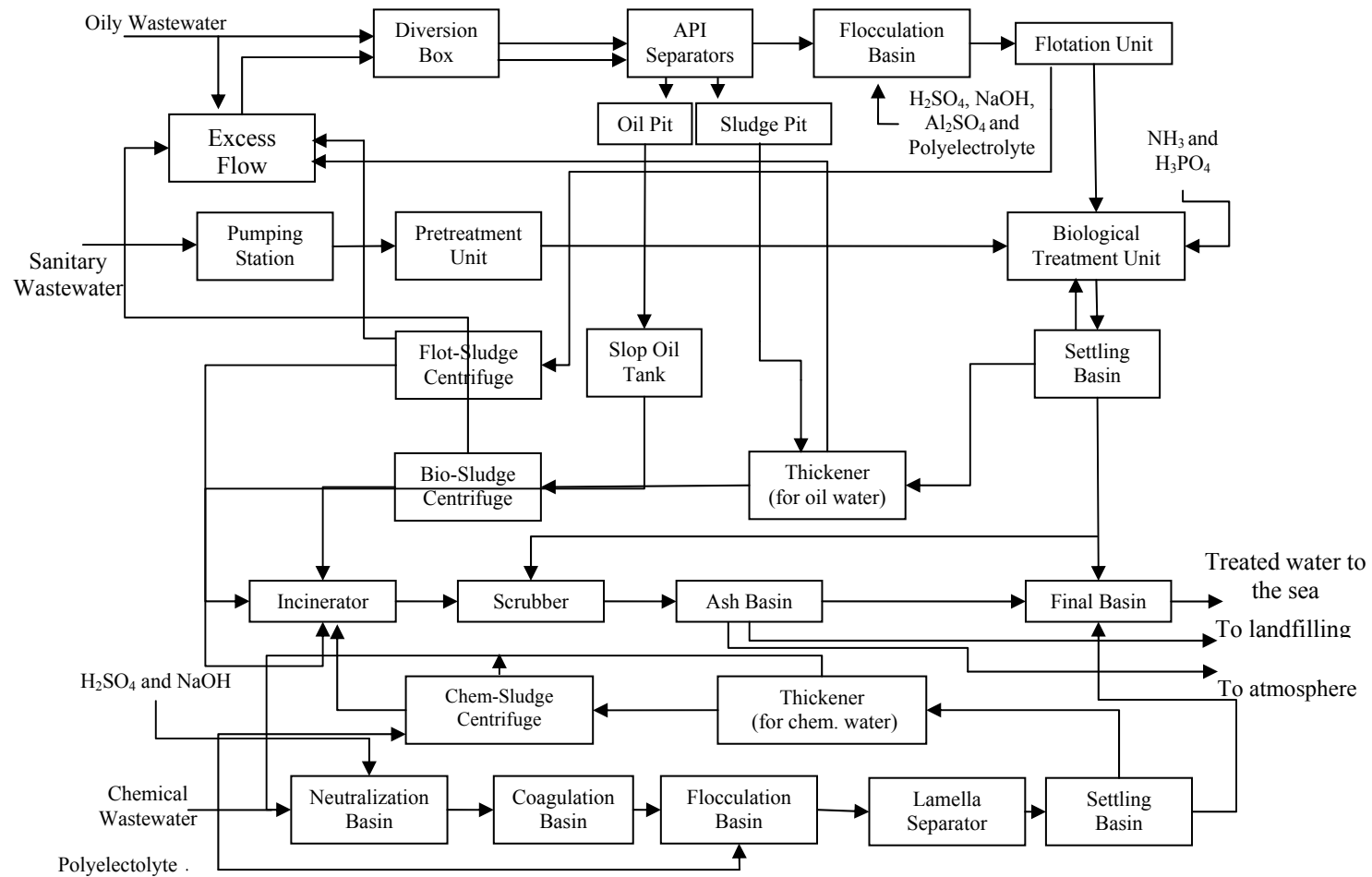


**Figure 2.6:** Petkim petrochemical complex wastewater treatment plant

## 2.6 Disposal Methods of Sewage Sludge

Sludge disposal is a worldwide problem and a wide variety of disposal routes have been adopted as dictated by local conditions. The final resting place of the sludge must be either on the land, in the air or in the water. The technologies utilized for sludge disposal as well as the environmental effects incurred are dictated largely by the choice of final resting place.

Disposal of sewage sludge to land is widely practiced, but is coming under increasing pressure as suitable sites become less and less available and controls on toxic materials become more stringent. Both landfill operations and application to agricultural soil are practiced, the main limitations arising from such factors as: pathogens, heavy metals, toxic organics and transport and application difficulties. A variety of technologies is available to circumvent these difficulties however, sometimes, at considerable cost. Present research is indicating that while organochlorines at low concentrations in the soil do not transfer to crops and are eventually degraded by soil microorganisms, heavy metals do accumulate and have a significant transfer to the food chain. For this disposal route, a cost effective means for removing heavy metals from sludge is required.

Disposal of sludge to the air largely employs high temperature incineration or pyrolysis. Incineration converts all the organic matter in the sludge to carbon dioxide and leaves behind most of the inorganic material as a dry ash. Pyrolysis, on the other hand, produces a liquid hydrocarbon as well as CO<sub>2</sub> and ash. In some circumstances the liquid hydrocarbon can be used directly as a diesel fuel. However, all high temperature processes are very capital intensive and require considerable add on equipment, such as stack gas scrubbers, to prevent gross air pollution. Because of its high volatility, mercury is difficult to remove from stack gas emissions.

Digestion of sludge uses anaerobic bacteria to break down between 30 and 40% of the organic matter to form a gaseous mixture of methane/CO<sub>2</sub> in the ratio of about 3:1. This operation is widely practiced in order to "stabilize" the sludge before final disposal. It is a relatively simple process to engineer and produces a valuable energy source in the methane containing offgas. As conventionally practiced, anaerobic digestion of sewage sludge converts

only about 30% of the organic matter to methane and carbon dioxide. Although this reduction is sufficient to "stabilize" the sludge, a large volume remains for disposal. There are a number of ways to significantly increase the conversion of organic matter to methane in anaerobic digesters. Those methods need to be further researched as they promise a great reduction in subsequent sludge handling problems.

Disposal of sewage sludge to the ocean has been widely practised, but is now coming under increasing pressure to be banned because of its perceived environmental effects. However, the results of sludge dumping appear to be very site specific and are influenced heavily by the range of constituents in the sludge. Materials of concern are organic matter, oil and grease, bacteria and virus, heavy metals, organochlorines and nutrients such as nitrate and phosphate. In well flushed and dispersive ocean environments the major concern is organochlorines, which do accumulate up the food chain and can cause severe health problems in higher species. On the other hand heavy metals, when present at low concentrations, do not appear to accumulate through the ocean food chain. Mercury levels in swordfish and tuna do not appear to have increased during the last fifty years. Fish are able to sequester and purge low levels of heavy metals by use of the enzyme metallothionein. In enclosed coastal seas with restricted circulation the major environmental problem is eutrophication caused by the addition of nutrients. Organic matter, oil and grease and pathogens generally cause problems only when discharged close to beaches or shell fisheries.

Though, large amount of this sewage sludge is disposed of by landfilling after dewatering, such landfill poses a serious problem in terms of pollution control and difficulties in finding available space within in a reasonable distance of large pollution areas, incineration is commonly employed to reduce the sludge volume. However, the operational cost is high since a great deal of energy is required to vaporize the water present; thus there is an urgent demand for a new approach to sludge disposal.

Under such circumstances, research and development programmes have been initiated for utilization of sewage sludge as a usable energy source, and new process such as pyrolysis, combustion, gasification and extraction have been proposed. For the production of liquid fuels and as a means of pollution control sewage sludge has directly converted into heavy oils. (Bridgewater, A. V., 2003)

## 2.7 Current Biomass Conversion Technologies

Biomass energy is one of humanity's earliest sources of energy particularly in rural areas where it is often the only accessible and affordable source of energy. Typical solid wastes include wood material, pulp and paper industry residues, agricultural residues, organic municipal material, sewage, manure, and food processing by-products. Worldwide biomass ranks fourth as an energy resource, providing approximately 14% of the world's energy needs. All human and industrial processes produce wastes, that is, normally unused and undesirable products of a specific process. Biomass is considered one of the main renewable energy resources of the future due to its large potential, economic viability and various social and environmental benefits. It was estimated that by 2050 biomass could provide nearly 38% of the world's direct fuel use and 17% of the world's electricity.

Main current biomass technologies are:

- Destructive carbonization of woody biomass to charcoal
- Gasification of biomass to gaseous products
- Pyrolysis of biomass and solid wastes to liquid, solid and gaseous products
- Supercritical fluid extractions of biomass to liquid products
- Liquefaction of biomass to liquid products
- Hydrolysis of biomass to sugars and ethanol
- Anaerobic digestion of biomass to gaseous products
- Biomass power for generating electricity by direct combustion or gasification and cofiring of biomass with coal
- Biological conversion of biomass and waste (biogas production, wastewater treatment)
- Biomass densification (briquetting, pelleting)
- Domestic cookstoves and heating appliances of fuelwood
- Biomass energy conservation in households and industry
- Solar photovoltaic and biomass based rural electrification
- Conversion of biomass to a pyrolytic oil (biofuel) for vehicle fuel
- Conversion of biomass to methanol and ethanol for internal combustion engines

There are four major methods for conversion of organic wastes to synthetic fuels: (1) hydrogenation; (2) pyrolysis; (3) gasification; and (4) bioconversion. The first three have been

advanced to the pilot-plant stage, while the fourth has been the subject of only minor research effort, but is a long term possibility. (Figure 2.7)

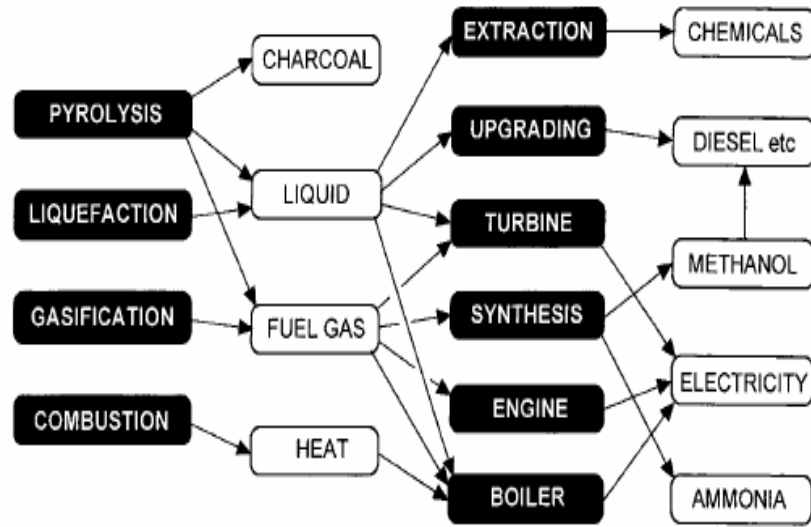


**Figure 2.7:** Products from thermal biomass conversion

### 2.7.1 Gasification of Biomass

Gasification is a form of pyrolysis, carried out at high temperatures in order to optimize the gas production. The resulting gas, known as producer gas, is a mixture of carbon monoxide, hydrogen and methane, together with carbon dioxide and nitrogen. Biomass gasification technologies have historically been based upon partial oxidation or partial combustion principles, resulting in the production of a hot, dirty, low calorific value gas that must be directly ducted into boilers or dryers. In addition to limiting applications and often compounding environmental problems, these technologies are an inefficient source of usable energy. Biomass gasification is the latest generation of biomass energy conversion processes, and is being used to improve the efficiency, and to reduce the investment costs of biomass electricity generation through the use gas turbine technology. High efficiencies (up to about 50%) are achievable using combined-cycle gas turbine systems, where waste gases from the gas turbine are recovered to produce steam for use in a steam turbine. Economic studies show that biomass suffocation plants can be as economical as conventional coal-fired plants.

### 2.7.1.1 Steam Reforming of Biomass

Most biomass gasification systems utilize air or oxygen in partial oxidation or combustion processes. These processes suffer from low thermal efficiencies and low calorific gas because of the energy required to evaporate the moisture typically inherent in the biomass and the oxidation of a portion of the feedstock to produce this energy. The process of synfuels from biomass will lower the energy cost, improve the waste management and reduce harmful emissions.

The molecules in the biomass (primarily carbon, hydrogen and oxygen) and the molecules in the steam (hydrogen and oxygen) reorganize to form syngas. The hydrogen and oxygen molecules in the steam are liberated and a series of reactions result in a reorganization of the compounds to form synthesis gas (primarily  $H_2$ ,  $CO$  and  $CO_2$ ). This synthesis gas is then catalytically converted into methanol, ammonia or another product.

### 2.7.2 Pyrolysis of Biomass

Pyrolysis is defined as the thermal destruction of organic materials in the absence of oxygen. Pyrolysis is the basic thermochemical process for converting biomass to a more useful fuel (Figure 2.8). Biomass is heated in the absence of oxygen, or partially combusted in a limited oxygen supply, to produce a hydrocarbon rich gas mixture, an oil-like liquid and a carbon rich solid residue.

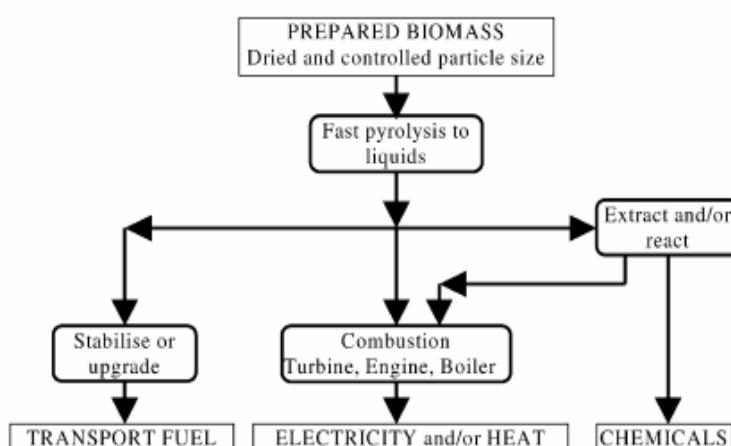


**Figure 2.8:** Applications for bio-oil

In pyrolysis process, biomass converts into liquid (bio-oil or bio-crude), charcoal and non-condensable gases, acetic acid, acetone, and methanol by heating the biomass to about 750 K in the absence of air. The process can be adjusted to favor charcoal, pyrolytic oil, gas, or methanol production with a 95.5% fuel-to-feed efficiency.

Pyrolysis can be used for the production of bio-oil if flash pyrolysis processes are used and are currently at pilot stage. Some problems in the conversion process and use of the oil need to be overcome; these include poor thermal stability and corrosivity of the oil. Upgrading by lowering the oxygen content and removing alkalis by means of hydrogenation and catalytic cracking of the oil may be required for certain applications. Comparison of pyrolysis and liquefaction processes is given in Table 2.12.

**Table 2.12:** Comparison of liquefaction and pyrolysis

| Process      | Temperature (K) | Pressure(MPa) | Drying      |
|--------------|-----------------|---------------|-------------|
| Liquefaction | 525-600         | 5-20          | Unnecessary |
| Pyrolysis    | 650-800         | 0.1-0.5       | Necessary   |

Temperature ranges for different compounds in matter must be evaluated before thermal processes. (Table 2.13)

**Table 2.13:** Temperature ranges for different compounds to decompose

| Groups of Compounds Decomposed | Temperature range (°C) |
|--------------------------------|------------------------|
| Moisture                       | up to 150              |
| Carboxylic                     | 150–600                |
| Phenolic                       | 300–600                |
| Ether oxygen                   | up to 600              |
| Cellulosic                     | up to 650              |
| Oxygen containing compounds    | 150–900                |

### 2.7.3 Co-firing of Biomass and Coal Blends

Co-firing refers to the combustion of biomass and coal for power production. Co-firing biomass with coal, in comparison with single coal firing, helps reduce the total emissions per unit energy produced. Co-firing biomass with coal has the capability to reduce both  $\text{NO}_x$  and  $\text{SO}_x$  levels from existing pulverized-coal fired power plants. Co-firing may also reduce fuel costs, minimize waste and reduce soil and water pollution depending upon the chemical composition of the biomass used. As such, the air pollution emissions accompanying the coal combustion are significant. Among these pollutants are oxides of sulfur ( $\text{SO}_x$ ) and nitrogen ( $\text{NO}_x$ ), which lead to acid rain and ozone depletion. In addition, greenhouse gas emissions ( $\text{CO}_2$ ,  $\text{CH}_4$ , etc.) have become a global concern. Numerous methods have been proposed for reducing gaseous emissions of  $\text{SO}_2$ ,  $\text{NO}_x$  and  $\text{CO}_2$  from fossil fuel combustion and for reducing costs associated with these mitigation techniques. Recent studies have shown that burning biomass with fossil fuels has a positive impact both on the environment and the economics of power generation. The emissions of  $\text{SO}_2$  and  $\text{NO}_x$  were reduced in most cofiring of biomass and coal techniques.

## 2.8 Supercritical Fluid Extraction of Sewage Sludge

SCFs have both gas and liquid like properties. They possess gas like mass transfer properties and the solvation characteristics of liquids. Their high diffusivity allows them to penetrate solid materials, and their liquid like densities enable them to dissolve analytes from a solid matrix. SCFs are compressible, and small pressure changes produce significant changes in their density and in their ability to solubilise compounds. Also, SCFs have almost no surface tension. Thus, they can penetrate low porosity materials. In addition, their very low viscosity provides favorable flow characteristics. These properties enable SCFs to provide excellent extraction efficiency and speed.

The combined gas like mass transfer and liquid like solvating characteristics of SCFs have led to considerable excitement for their use as mobile phases for SCF chromatography, but their use for analytical scale extraction has only recently received attention. SCFs are sometimes considered to be 'super solvents', but this is not true when their solvating power is compared with that of liquids. SCFE methods add a new dimension to the usual solvent

properties: the variable fluid density. The fluid density and, with it, the solvent power and selectivity undergo drastic changes with moderate changes of temperature and pressure in the critical region. The solvent strengths of SCFs approach those of liquid solvents only as their density is increased, and the maximum solubility of an organic compound is frequently higher in liquid solvents than in SCFs. The concentration in the gas phase of substances of rather low volatility increases sharply at temperatures close to the gas critical value when the critical pressure of the gas is approached or exceeded. Other attractive properties of SCFs are: lower viscosity and surface tension and higher diffusivities than conventional liquid solvents.

Supercritical fluid extraction is a fast and efficient method to extract all manner of organic compounds from a wide variety of solid sample matrices. Due to the marked change in its polarity with temperature, water is an interesting alternative to carbon dioxide as the extraction fluid. By merely adjusting the temperature, selectivity can be achieved for inorganic or organic compounds and for polar or non-polar organic compounds. Many organic compounds are sufficiently soluble to be extracted under subcritical conditions and, in this way, instrumental and other problems, such as the high corrosiveness of supercritical water, can be avoided. Instrumentation for sub- and supercritical water extraction was developed and modified in several ways with the aim of simplifying the procedure while maintaining good recoveries. Relative to Soxhlet extraction, recoveries were higher or similar when solid-phase and liquid collections were combined.

## 2.9 Soxhlet Extraction

The Figure 2.9 shows a design of glassware for Soxhlet extraction of compounds using solvents. The glassware shown consists of the following;

1. Round bottom flask for boiling the solvent.
2. Soxhlet extractor body for collecting the solvent as it is distilled and extracting the compounds of interest out of the thimbles. The type shown opposite has a ground glass tapered socket at the top restricting the size of samples used and is used for lower siphoning volumes.
3. Condenser for refluxing, different types available.

Soxhlet extractors are used for continuous extraction of analytes from a solid into an organic solvent. As the flask containing the solvent is heated, vapors rise in the larger outside tube, enter the water-cooled condenser and reliquify. When the liquid level in the extractor reaches the top of the bent tube, siphoning action returns the extract-enriched solvent to the flask.



**Figure 2.9:** Soxhlet extraction apparatus

## 2.10 Liquid Absorption Chromatography

- In column chromatography separation methods, liquid mixtures are separated into fractions with adsorption–desorption tendency on the adsorbent material (silica-alumina).
- Liquid mixtures are poured from the top of the glass column filled with adsorbent material.
- Every fraction adsorbs onto material at different heights.

- When proper desorbent (elution solvent) is poured into column, every fraction left from column with different velocities.
- Fractions eluted faster moves toward the bottom part of the column and leaves from the column as a first. This depends on the polarity of the solvent.

The expected elution order of organic classes was given in Figure 2.10.

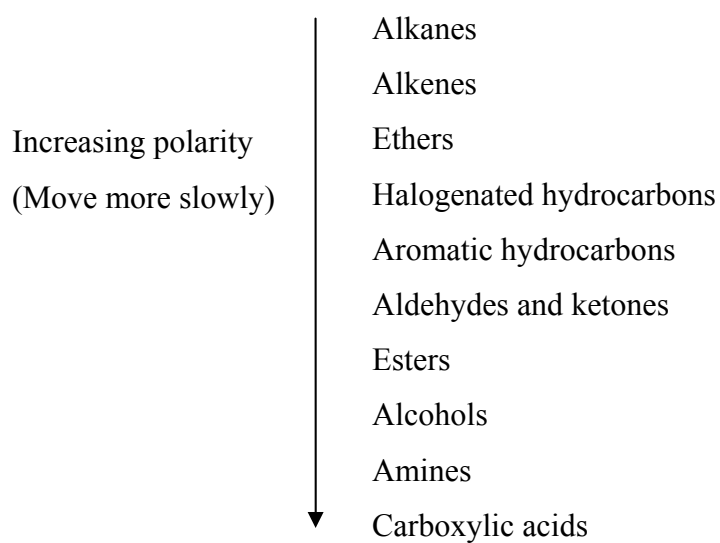


**Figure 2.10:** The expected elution order of organic classes

### 3. LITERATURE REVIEW

Sewage sludge is produced in significant quantities when municipal and industrial wastewater effluents are treated by biological processes. The cost of disposal of these sludges has increased greatly in recent years, and it has been estimated that the disposal costs are in the order of 50% of the total wastewater treatment costs. The major fates of sewage sludge are agricultural utilization, incineration, landfill and ocean disposal. Sludges of industrial origin are often high in heavy metals, thereby ruling out land application. The availability of landfill sites is extremely limited for most municipalities so the major form of sludge disposal is incineration, which is expensive. However, the operational cost is high since a great deal of energy is required to vaporize the water present; thus there is an urgent demand for a new approach to sludge disposal. (Konar et al., 1994)

The increased costs of waste disposal, and growing environmental concern about it, have prompted investigation of alternate technologies for sludge disposal. One of these technologies is thermal conversion to yield liquid fuel products and chemical feedstocks.

The conversion of sludge to fuel products has been known for more than six decades. The German work has demonstrated that a synthetic crude oil could be produced from a sewage sludge by heating at 300-350°C in an oxygen free environment for about 30 min. Campbell et al. have developed technology for the thermal liquefaction of sewage sludge based on these German results. Piskorz et al. have reported the flash pyrolysis of sewage sludge, in which a dried mixture of raw and activated sludge was pyrolysed in a bench scale fluidized bed reactor at residence times less than 1 s over a temperature range of 400-700°C. (Piskorz et al., 1986)

The direct thermomechanical liquefaction of sewage sludge without a reducing agent has been investigated by Molton et al. They developed a process in which dewatered sewage sludge was heated with sodium carbonate above 250°C in a nitrogen environment in a continuous flow mode. (Molton et al., 1985)

Recent research showed that the major mechanism by which oil is produced from the thermal treatment of sewage sludge is one involving distillation of lipids. The lipids were concluded to be the major precursor of useful oil. Oil is also derived from protein. However, this protein gives rise to high amounts of nitrogen and sulfur in the pyrolysis oils and is, therefore, a nuisance. Hence selective separation and pyrolysis of the lipid fraction would lower the nitrogen and sulfur content in the oils. The lipid fraction contains hydrocarbons, triglycerides and straight chain carboxylic acids. Raw sludges are high in carboxylic acid content, whereas in digested sludges most of the carboxylic acids have been biodegraded. Therefore, the oil yields from raw sludges are higher than those from digested sludges. In addition, the catalytic hydrogenation of carboxylic acids to yield hydrocarbons is virtually impossible. Based on these observations, Konar et al. investigated the catalytic pyrolysis of sewage sludge lipids. This work reported the pyrolysis of toluene-extracted lipids from raw sewage sludge over activated alumina at 450°C. The liquid product has a great potential to be used as diesel fuel, heating fuel and chemical feedstocks. (Konar et al., 1994)

Direct liquefaction of sewage sludge results in a foul-smelling viscous liquid which has high nitrogen and sulfur content. Boocock et al. confirmed that an appreciable amount of nitrogen is present in sewage sludge due to the proteins and nucleic acids from original waste and dead microorganisms. They showed that the lipid fraction is the major source of useful hydrocarbons. The lipid fraction of a typical raw sludge was found to contain 65% straight chain carboxylic acids, 28% unsaponifiables, and 7% triglycerides. They performed the pyrolysis of sewage sludge lipid, a carboxylic acid-rich substrate and canola oil (a triglyceride) over activated alumina at 450°C and atmospheric pressure. Liquid products showed a uniform concentration across the C<sub>6</sub> to C<sub>17</sub> mass range, whereas for diesel fuel a distribution across the C<sub>10</sub> to C<sub>19</sub> mass range is common. (Boocock et al., 1995)

Yokoyama et al. have reported an advanced treatment of sewage sludge by direct thermochemical liquefaction. All these pyrolysis processes, although performed under different experimental conditions, yielded liquid products which contained significant amounts of oxygenated compounds and unacceptable amounts of nitrogen and possibly sulfur. Yokoyama et al. studied the conversion of sewage sludge (having a moisture content of 75 wt %) into liquid fuels in the presence of sodium carbonate under nitrogen atmosphere over the

temperature range 250-340°C. They obtained liquid fuels having heating values of ~33 MJ/kg were separable from an aqueous phase in high yields. (Yokoyama et al., 1987)

Kuriakose et al. reported the data obtained to utilize the waste sludge of a petroleum refinery in India. About 17 wt% of a lighter oil fraction can be recovered from this sludge and the characterization of the lighter oil is such that can be used as diesel fuel by blending with other appropriate refinery streams. (Kuriakose et al., 1994)

Fullana et al. have been studied on pyrolysis products at 850 °C of seven different types of sewage sludge. The main objective of this work has been the identification of the major number of possible hazardous organic pollutants in sewage sludge combustion and to find a relation between these compounds and the treatment that has been performed to the waste prior to pyrolysis. Three types of compound have been classified: CO<sub>2</sub>, light hydrocarbons and semivolatile compounds. (Fullana et al., 2003)

Kaminsky et al. has been pyrolyzed digested, thermally conditioned and dried sewage sludge in an indirectly heated fluidized bed reactor at temperatures ranging from 620°C to 750°C. A quantity of up to 40 kg of sewage sludge per hour has been converted into pyrolysis gas, oil, product water and carbonaceous residues in a continuously working pilot plant. The main constituents of the pyrolysis gas are hydrogen, methane, ethane, ethene and propene as well as carbon monoxide and carbon dioxide. The oil fraction yielded contains up to 30% aromatic compounds. The heavy metals from the sewage sludge become to a large extent enriched in the solid residue on account of the reducing conditions of the pyrolysis process. (Kaminsky et al., 1989)

The products obtained by primary and secondary pyrolysis of sewage sludges were studied. The primary pyrolysis was performed in a Pyroprobe 1000 analytical apparatus, connected in series to a secondary reactor and a gas chromatograph. The products analyzed were carbon oxides, water and several hydrocarbons, and the authors conclude that with this technique, a total gas yield as high as 46 wt% can be obtained, and that the pyrolysis is an adequate way of characterizing of this type of materials. (Caballero et al., 1997)

Pyrolysis of activated sewage sludge was investigated under inert conditions in a fluidised-bed to study the effects of temperature and gas residence time on the product distribution and composition with an aim to maximise the oil yield. The temperature was varied from 300 to 600°C and the gas residence time from 1.5 to 3.5 s. Three groups of products were produced, namely, a non-condensable gas phase, a solid phase (char) and a liquid phase (oil). A maximum of 30% oil yield (wt% daf of sludge fed) was achieved at a pyrolysis temperature of 525°C and a gas residence time of 1.5 s. The results from the oil analysis using GC–MS and H-NMR suggests that the structure of sewage sludge oil is made up of a group of aromatic clusters with one to three aromatic rings connected by long straight chain hydrocarbons with hydroxyl groups. (Shen., 2003)

Anaerobic biodegradation of the nonionic surfactants nonylphenol polyethoxylates (NPEs) in sewage sludge leads to the formation of higher concentrations of 4-nonylphenol (4-NP). The persistent contaminant, 4-NP, in the environment has recently been of increasing concern due to its toxic and estrogenic effects. Therefore, it is necessary to develop an effective treatment method for sewage sludge containing the environmentally threatening 4-NP before disposal into the environment. Recently, supercritical fluid extraction (SFE) has been found to be a better alternative to the conventional liquid solvent extraction methods (Soxhlet and sonication) for the extraction of environmental samples. This is due to several advantages such as rapid extraction, low solvent requirement, low cost and higher efficiency. The most popular fluid for SFE has been CO<sub>2</sub> because of its low critical properties ( $T_c$ :32°C,  $P_c$ :72 bar), high purity, low toxicity and cost, chemical inertness, and its ability to solvate a wide range of organic compounds including those having higher molecular mass. However, the limitation of CO<sub>2</sub> is that it is unable to extract the polar organic solutes quantitatively from the environmental samples even though the solutes are soluble in supercritical CO<sub>2</sub>. This shows that the extraction of polar molecules requires an addition of modifiers or co-solvents to the carbon dioxide. The commonly used modifier in SFE is methanol. When the temperature was increased from 40–60°C, there was a significant decrease in the recovery and when the temperature was further increased to 100°C the recovery is greater than 90%. This could be explained by the fact that the increase in the recovery after a certain level of temperature is due to the increase in the fluid diffusion coefficient. It was also noted that longer extraction time resulted in a low recovery. (Lin et al., 1999)

## 4. MATERIAL AND METHOD

In this section, some properties of sewage sludge produced from wastewater treatment unit in Petkim Petrochemical Complex were identified. Also, sequence of the experimental procedure of Soxhlet and supercritical fluid extraction processes were outlined. Characterization of products was carried out with different analysis techniques such as gas chromatography, column chromatography, IR, etc.

### 4.1. Material

#### 4.1.1. Sewage Sludge Produced from Petkim Wastewater Treatment Plant

Sewage sludge used in experiments is obtained from Petkim Petrochemical Complex wastewater treatment plant where 550 m<sup>3</sup> of oily, 120 m<sup>3</sup> of sanitary and 1000 m<sup>3</sup> of chemical wastewater are treated hourly. But, used sludge is a mixture of effluents of flotation sludge centrifuge and biological sludge centrifuge that are the final treatment equipments of oily wastewater and sanitary wastewater, respectively.

Some properties of effluent of flotation sludge and biological sludge centrifuge are given in Table 4.1 and 4.2.

**Table 4.1:** Effluent of flotation sludge centrifuge

|                    |                       |
|--------------------|-----------------------|
| Flow rate          | 2.4 m <sup>3</sup> /h |
| pH                 | 7                     |
| Temperature        | Ambient               |
| Dry Matter Content | 2.5% wt. (75 kg/h)    |

Table 4.1 continued

|                                                |                                                                                                    |
|------------------------------------------------|----------------------------------------------------------------------------------------------------|
| <b><u>Dry matter composition:</u></b>          |                                                                                                    |
| Oil                                            | 36% wt.                                                                                            |
| Solids                                         | 64% wt.                                                                                            |
| Solids quality                                 | Colloidal Floccs, originated with the addition of $\text{Al}_2(\text{SO}_4)_3$ in aqueous solution |
| Sludge specific gravity (wet)                  | 1.1                                                                                                |
| <b><u>Performance: (Dehydrated sludge)</u></b> |                                                                                                    |
| Dry matter content                             | 10-15% wt. min.                                                                                    |
| Dry solid separation efficiency                | 95%                                                                                                |

Table 4.2: Effluent of biological sludge centrifuge

|                                       |                       |
|---------------------------------------|-----------------------|
| Flow rate                             | 7.6 m <sup>3</sup> /h |
| pH                                    | 7                     |
| Temperature                           | Ambient               |
| Dry Matter Content                    | 2% wt. (160 kg/h)     |
| <b><u>Dry matter composition:</u></b> |                       |
| Oil                                   | 3% wt.                |
| Solids                                | 97% wt.               |
| Solids quality                        | Biological Floc.      |
| Sludge specific gravity (wet)         | 1.1                   |

Table 4.2 continued

| <b><u>Performance: (Dehydrated sludge)</u></b> |              |
|------------------------------------------------|--------------|
| Dry matter content                             | 11% wt. min. |
| Dry solid separation efficiency                | >95%         |

Firstly, samples were dried under sunlight so as to lower the moisture content to 4.5 wt %. Next, samples were broken into smaller pieces by jaw breaker and disc grinder. Sieve analysis of the sludge was performed and average particulate dimension is found to be 0.5 mm. After this analysis, samples were dried in a vacuum oven (at 40°C and 10 mmHg) until their weights stay constant and its moisture content is calculated. Also, sludge samples were combusted in an oven at 550°C for 2 hours to be able to determine its ash content. Elemental analysis of sewage sludge (C, H, and N) was performed by Carlo Erba 1106 Elemental Analyzer in Marmara Research Center. Higher heating value (HHV) and lower heating value (LHV) of this sludge were calculated by combusting sludge in a Calorimeter Bomb. Some properties of dewatered sewage sludge were tabulated in Table 4.3.

**Table 4.3:** Properties of dewatered sewage sludge

| <b><u>Sludge properties</u></b>              | <b><u>Value</u></b>  |
|----------------------------------------------|----------------------|
| Moisture content (wt %)                      | 4.5                  |
| Heating value <sup>a</sup> (kJ/kg)           | 16864                |
| Organics <sup>a</sup> (wt %)                 | 75.8                 |
| Ash (%)                                      | 24.2                 |
| <b><u>Elemental analysis<sup>b</sup></u></b> | <b><u>(wt %)</u></b> |
| C                                            | 53                   |
| H                                            | 7.8                  |
| N                                            | 4                    |

<sup>a</sup> On a dry basis

<sup>b</sup> On a dry and ash free basis

<sup>c</sup> Calculated by difference

Some of the trace elements in sewage sludge were identified by atomic absorption spectroscopy. Inorganic content and trace elements in sewage sludge are outlined in Table 4.4.

**Table 4.4:** Inorganic content and trace elements in sewage sludge (wt %)

| Content          | Amount (wt %) |
|------------------|---------------|
| SiO <sub>2</sub> | 9.82          |
| Cu               | 0.012         |
| Pb               | 0.11          |
| Ni               | 0.012         |

#### 4.1.2. Solvents

Different solvents that were acetic acid, tetrahydrofuran (THF), toluene, o-Xylene, pyridine, dichloromethane, acetone, tetraline isopropanol, carbon tetrachloride, carbon disulphide, cyclohexane, ethanol, n-hexane, methanol, cyclohexanol, water and mixture of dichloromethane and methanol (1/1, v/v) were used during Soxhlet extraction of sewage sludge.

Supercritical fluid extraction of sewage sludge was carried out by using water and toluene as solvents. After SCFE of sludge, Soxhlet extraction of sludge was performed by using THF and water content of extract removed by providing azeotropic mixture of THF and water in rotary evaporator. n-hexane was used to precipitate preasphaltenes. During liquid absorption chromatography process, n-hexane, toluene and methanol was used as elution solvents of oil into its aliphatic, aromatic and polar fractions.

#### 4.2 Method

Experimental studies were performed in two steps. In the first part, Soxhlet extractions of sewage sludge samples were carried out by using different solvents. According to total conversion of organic fractions in sewage sludge, appropriate solvents were selected and supercritical fluid extractions were carried out by using them. At the end of each run, washing and cleaning of autoclave were carried out with same solvents.

### 4.2.1 Soxhlet Extraction of Sewage Sludge

Soxhlet extraction of sewage sludge samples were carried out with different solvents which have different polarities. According to results obtained in Soxhlet extraction of sewage sludge, polar solvents have more prone to dissolve organic matter than non-polar.

### 4.2.2 Supercritical Fluid Extraction of Sewage Sludge and Experimental Procedure

Sewage sludge samples were ground to the desired particle size and dried in a vacuum oven (40°C and 10 mmHg). Extraction experiments were conducted in a 100 mL stainless steel autoclave rotation with 36 rev/min. Autoclave and its auxiliary were shown in Figure 4.1 and 4.2.

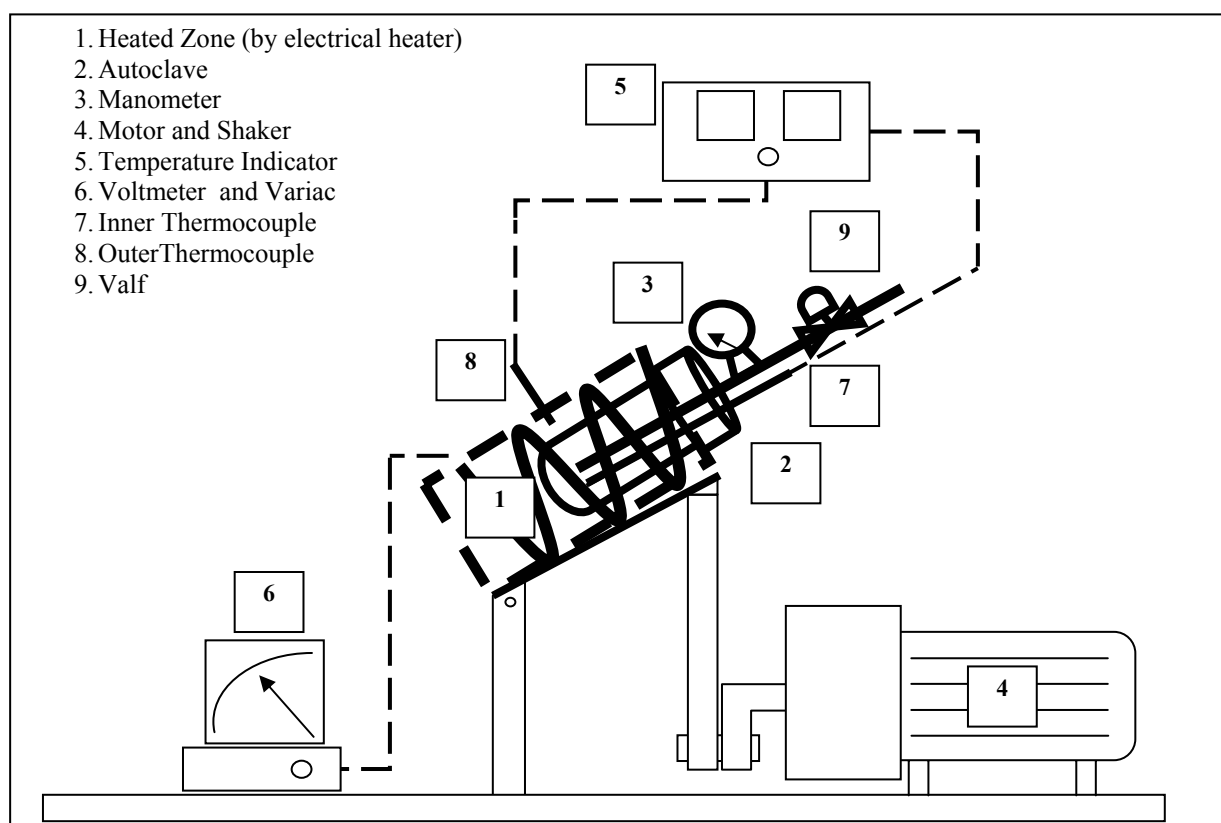


**Figure 4.1:** Schematic view of autoclave and its auxiliaries

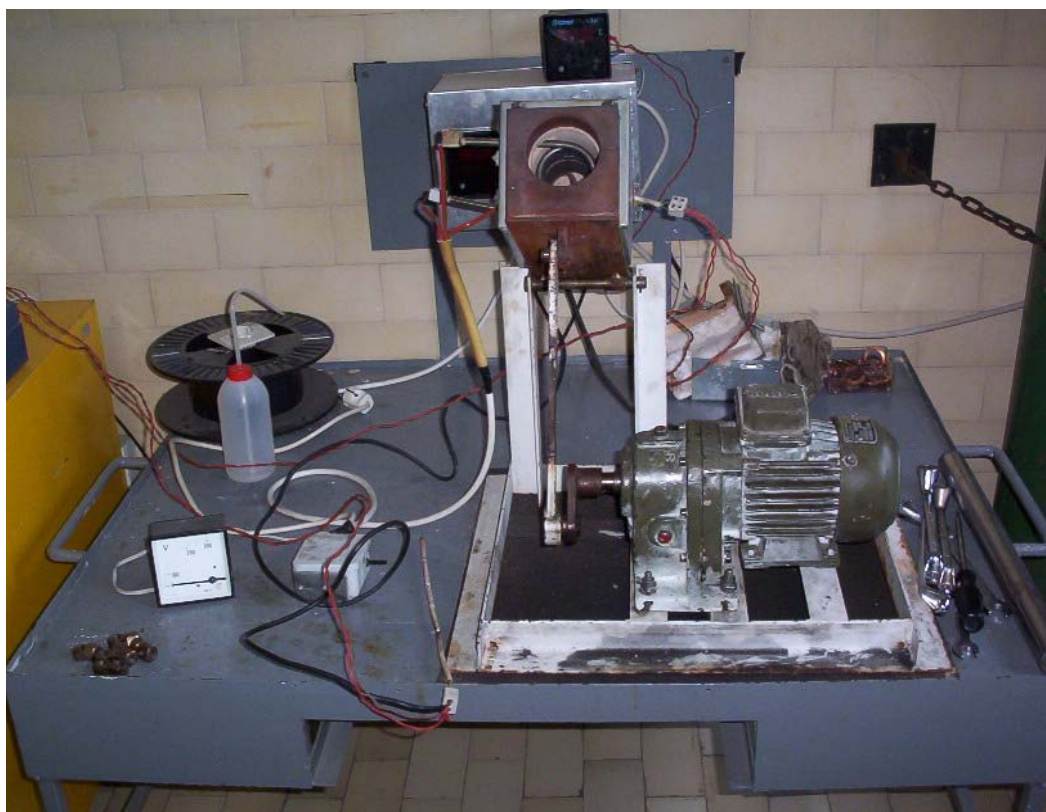


**Figure 4.2:** Autoclave and its auxiliaries

The autoclave was charged with different ratios of solvent/sludge. Water or toluene was used as supercritical fluids in these studies. Air was displaced from the autoclave with an inert gas ( $N_2$ ) stream before operation. The autoclave was heated to the desired temperature at a rate of  $6^\circ\text{C}/\text{min}$  and was held at this temperature during the operation. The experiments were performed at a temperature range of  $300\text{--}450^\circ\text{C}$  and for reaction times of 1h. At the end of each run, reactor was cooled down to ambient temperature by blowing cold air onto the surface of autoclave. Then, the valves on the reactor were opened and gaseous products of reaction were introduced to gas sampling bulbs (Figure 4.3), where the volume of gaseous products was measured. Gaseous products were analyzed by connecting gas sampling bulb with gas sampling valve of gas chromatography. The volume of sampling loop was 1cc.



**Figure 4.3:** Introducing gaseous products into gas sampling bulb

After the gaseous products were released from the reactor, inside of the reactor was washed with tetrahydrofuran (THF). This content was filtered to separate solid and liquid (extract) parts. The residual solid was placed in a Soxhlet thimble and extract was filled in a flask that includes suitable amount of THF (e.g. 196mL. of THF was required for removing 10 g of water). T-x-y diagrams for THF-water systems were given in Figure 4.4. Because, THF forms an azeotropic mixture (94.6 wt. % THF and 5.4 wt. % water) with water at 63°C and 1 atm., Soxhlet extraction was performed at this temperature for 6 h.

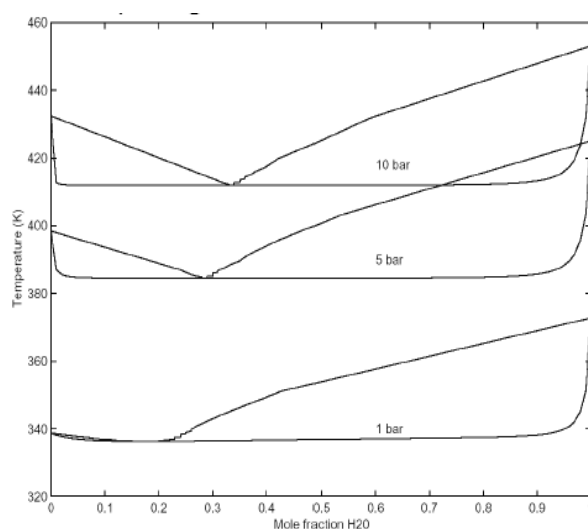


**Figure 4.4:** T-x-y diagrams for THF-water systems

After completion of extraction, thimble was taken from extractor and solid residue was conducted to the ash analysis. Liquid mixture in the flask which includes water, THF and extract was concentrated to 50 mL by rotary evaporator to remove water and THF.

As a result of this process, THF and water was separated from the extract which consists of oil, asphaltenes and preasphaltenes. Precipitation of asphaltenes and preasphaltenes out of extract was accompanied by dropping 500 mL of n-hexane. This solution was filtrated and insoluble parts are removed from oil. Also, precipitated parts were washed with toluene and toluene-soluble (asphaltenes) and toluene-insoluble (preasphaltenes) fractions were identified. n-hexane was removed from oil rich phase by means of a rotary evaporator at 50°C under vacuum and the weight of oil has been determined in this way. Sequence of experimental procedures and methods for product analysis are given in Figure 4.5.

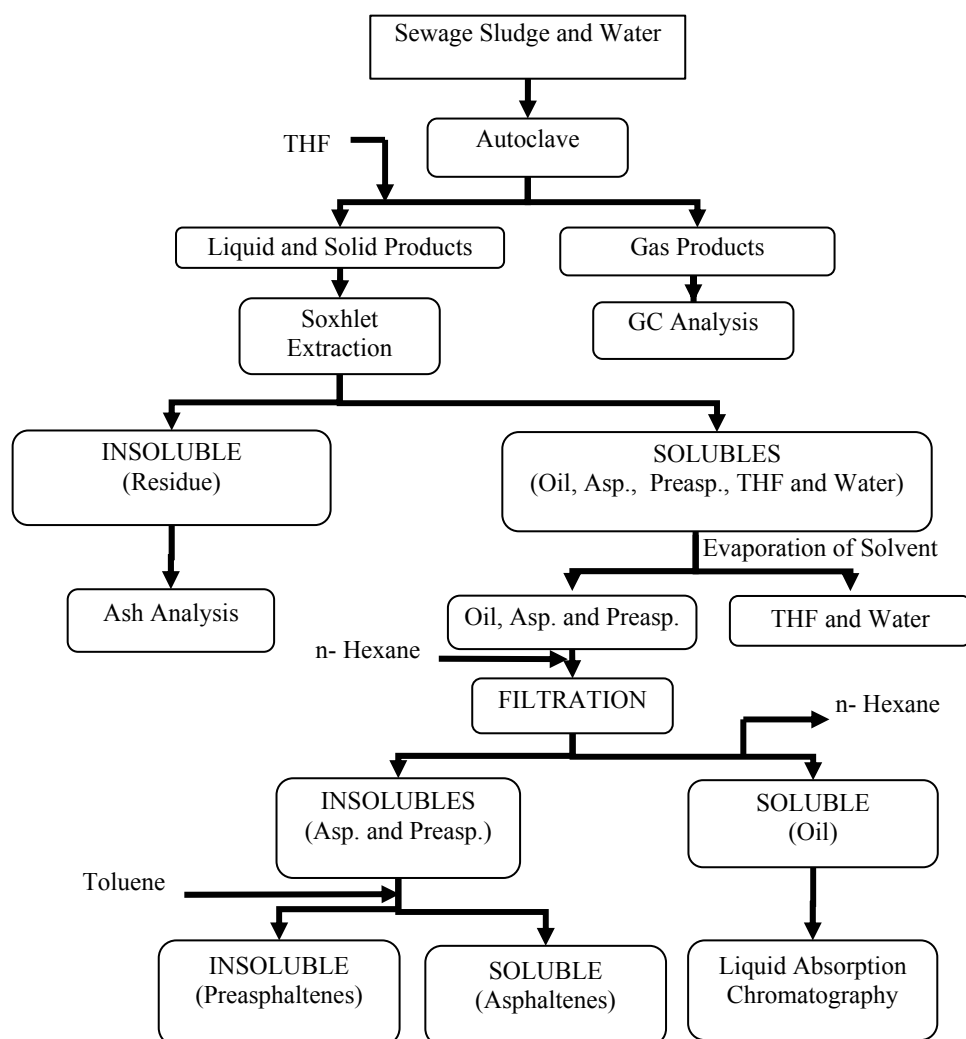


**Figure 4.5:** Sequence of Experimental Procedures and Product Analysis

### 4.2.3 Analytical methods

#### 4.2.3.1 Gas chromatography

The gaseous products were analyzed by three gas chromatographic systems that have different operating conditions. The separation of gases into individual compounds in the column was achieved by using carrier gas and detector. Operation conditions of these chromatography systems were given in Table 4.5, 4.6 and 4.7.

**Table 4.5:** Operating conditions of gas chromatography for H<sub>2</sub> analysis

| Analysis of H <sub>2</sub> |                                                |
|----------------------------|------------------------------------------------|
| Gas Chromatography         | HP 6890 Hewlett Packard                        |
| Column                     | 2.0 m x 1/8in. Molecular sieve 13X, 30-60 mesh |
| Carrier Gas                | Nitrogen, 20mL/min                             |
| Detector                   | TCD                                            |
| Detector Temperature       | 150°C                                          |
| Temperature Program        | Oven: 80°C isothermal                          |
| Injection Temperature      | 150°C                                          |

**Table 4.6:** Operating conditions of gas chromatography for CO<sub>2</sub> and C<sub>1</sub>-C<sub>6+</sub> analysis

| Analysis of CO <sub>2</sub> , C <sub>1</sub> -C <sub>6+</sub> |                                                                    |
|---------------------------------------------------------------|--------------------------------------------------------------------|
| Gas Chromatography                                            | Chrompack                                                          |
| Column                                                        | 2.0 m x 1/8in. Haysep N, 80-100 mesh                               |
| Carrier Gas                                                   | Hydrogen, 28mL/min                                                 |
| Detector                                                      | FID                                                                |
| Detector Temperature                                          | Filament: 185°C and Block: 135 °C                                  |
| Temperature Program                                           | Initially 105°C<br>3°C/min to 170°C<br>170°C isothermal for 20min. |
| Injection Temperature                                         | 150°C                                                              |

**Table 4.7:** Operating conditions of gas chromatography for CO analysis

| <b>Analysis of CO</b>           |                                                                                       |
|---------------------------------|---------------------------------------------------------------------------------------|
| Gas Chromatography              | HP 5890 Hewlett Packard                                                               |
| Column<br>(Connected in series) | 6.0 m x 1/8in. Propak Q, 50-80 mesh<br>2.0 m x 1/8in. Molecular sieve 13Q, 60-80 mesh |
| Carrier Gas                     | Hydrogen, 9 mL/min                                                                    |
| Detector                        | FID                                                                                   |
| Detector Temperature            | 200 °C                                                                                |
| Temperature Program             | Oven: 85°C isothermal                                                                 |
| Injection Temperature           | 150 °C                                                                                |

#### 4.2.3.2 Infrared Spectroscopy (IR)

IR spectroscopic analysis of deasphalted oil were evaluated to determine aliphatic/aromatic ratios. IR spectra (transmittance) of oils were taken between  $4000\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$  band positions by using Shimadzu 470 IR spectrophotometer. The peak integration of aliphatic stretching C–H bands ( $2800\text{--}3000\text{ cm}^{-1}$ ) and aromatic C–H out-of plane bending bands ( $600\text{--}900\text{ cm}^{-1}$ ) (Ballice and Larsen, 2003) were done by using numerical calculation.

#### 4.2.3.3 Liquid Absorption Chromatography

Liquid absorption chromatography was used to separate oil into aliphatic, aromatic and polar fractions by elution with n-hexane, toluene and methanol, respectively (Figure 4.6). (Özkan A.R et al., 1998). Elution solvents were poured into column according to their increasing polarities (that is dipole moments) that were 0 Debye for n-hexane, 0.36 Debye for toluene and 1.7 Debye for methanol at 20°C.

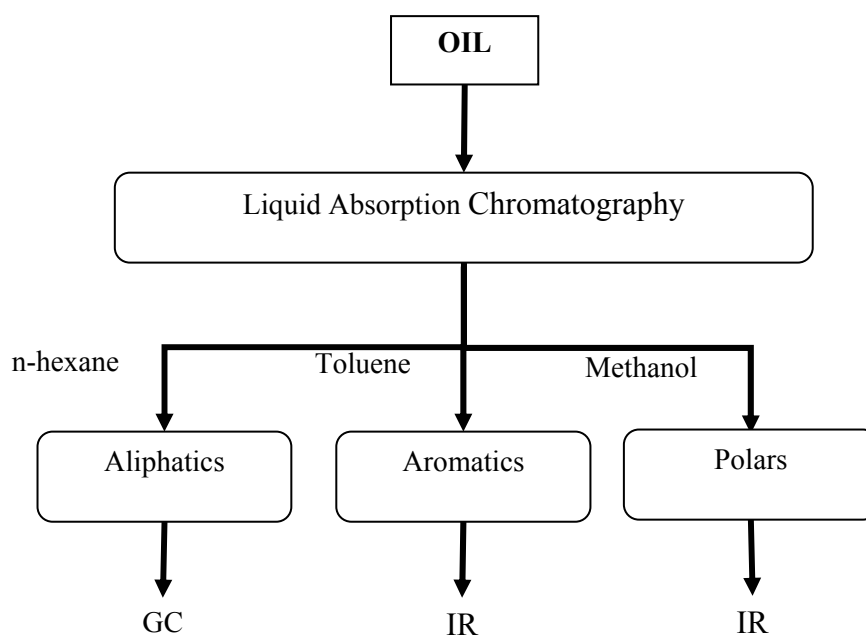


**Figure 4.6:** Liquid Absorption Chromatography

The oil fractions of extraction products were separated by liquid adsorption chromatography on a glass column (600mm x 3 mm i.d.). The lower part was packed with neutral silicagel (particle size 0.063-0.2 mm) which was activated at 120°C for 24 h. The upper part was packed with neutral aluminum oxide (particle size 0.063-0.2 mm) which was activated at 400°C for 8 h.

2 g of liquid products (deasphalted) was dissolved in hexane (3mL per g of sample) and applied to the adsorbent column wetted with hexane. The sample was eluted with the following series of mobile phases: 250 mL of n-hexane, 250 mL of toluene and 250 mL of methanol.

After removing the solvent content of each fraction in rotary evaporator, they were weighed for determination of weight fractions in oil.

According to retention time and boiling point of products simulated distillation curves of n-hexane eluted fractions were obtained and it was separated into gasoline, middle distillate

and wide-cut gas oil fractions. Detailed information on petroleum hydrocarbons are given in Table 4.8. n-hexane eluted fraction of deasphalted oil was analyzed by gas chromatography. The operating conditions of gas chromatography is given in Table 4.9.

**Table 4.8:** Distillation fractions of petroleum hydrocarbons

| Fraction          | Boiling Point (°C) | Carbon Number | Ingredients/Source                                                                                                |
|-------------------|--------------------|---------------|-------------------------------------------------------------------------------------------------------------------|
| Gasoline          | <200               | 4-12          | Straight-chain paraffins, branched-chain paraffins, alkylcyclopentanes, alkylcyclohexanes and alkylbenzenes.      |
| Middle Distillate | 185-345            | 12-20         | Alkyl naphthalenes, biphenyls and other PAHs. / Kerosene, diesel, heating oil, jet, rocket and gas turbine fuels. |
| Wide cut gas-oil  | 345-540            | 20-44         | - / waxes, lubricating oils and feedstock for catalytic cracking to produce gasoline.                             |
| Residue           | >540               | >44           | Asphalt (asphaltene, resin and oil similar to lubricating oil)                                                    |

**Table 4.9:** Operating conditions of gas chromatography for analysis of aliphatic fractions

| Analysis             | Aliphatic Fractions of Oil                                                      |
|----------------------|---------------------------------------------------------------------------------|
| Gas Chromatography   | HP 6890 Hewlett Packard                                                         |
| Column               | 100 m x 0.25 mm                                                                 |
| Stationary phase     | Cross-linked methylsiloxane, HP-1                                               |
| Carrier Gas          | Hydrogen, 30mL/min                                                              |
| Detector             | FID                                                                             |
| Detector Temperature | 350°C                                                                           |
| Temperature Program  | 40°C isothermal for 2 min.<br>5°C /min to 280°C<br>280°C isothermal for 40 min. |

Gas chromatograms of aliphatic fractions of oil, which was obtained by extraction of activated sludge with water at 350°C, were given in Figure 4.7 and 4.8. Gas chromatograms of aliphatic fractions of oil, which was obtained by extraction of activated sludge with toluene at 350°C, were given in Figure 4.9 and 4.10.

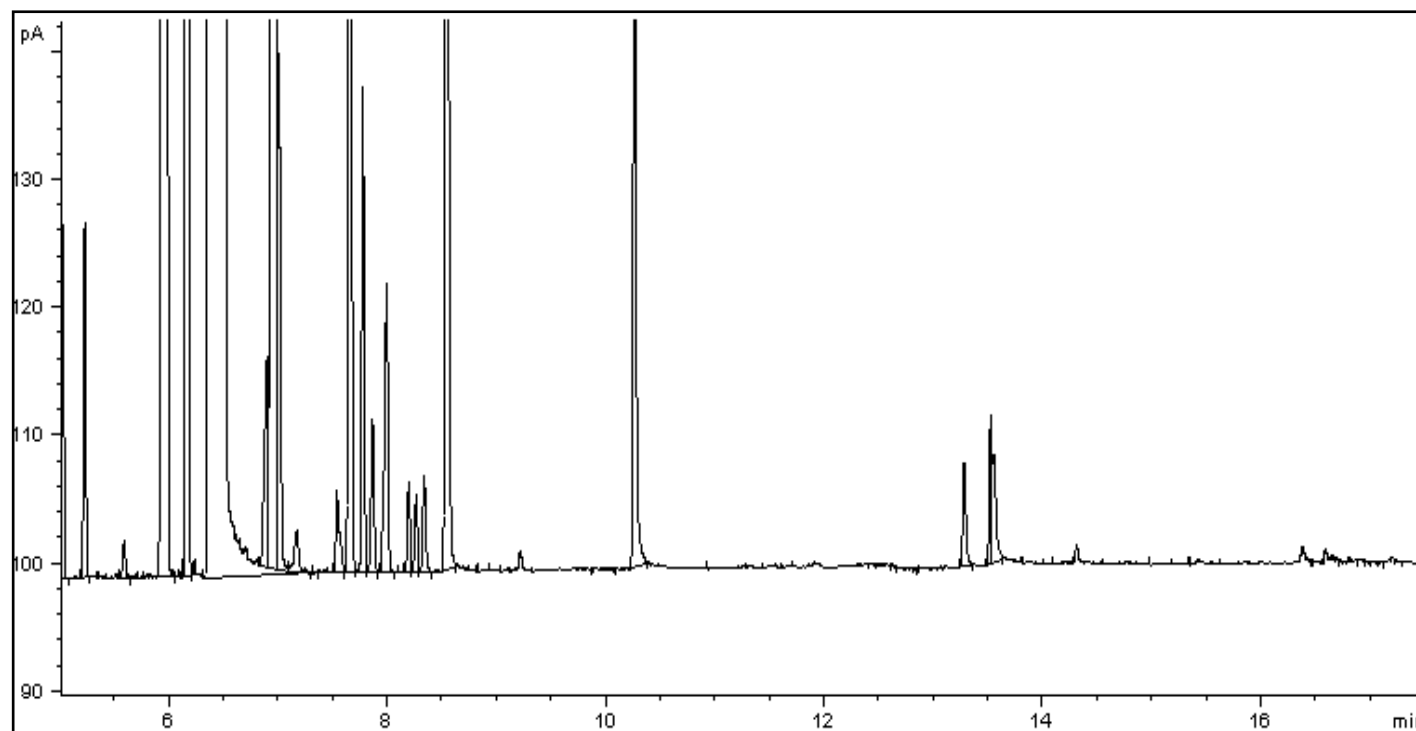


**Figure 4.7:** Gas chromatogram of aliphatic fraction of oil extracted with water at 350°C (5-17.5 min.)

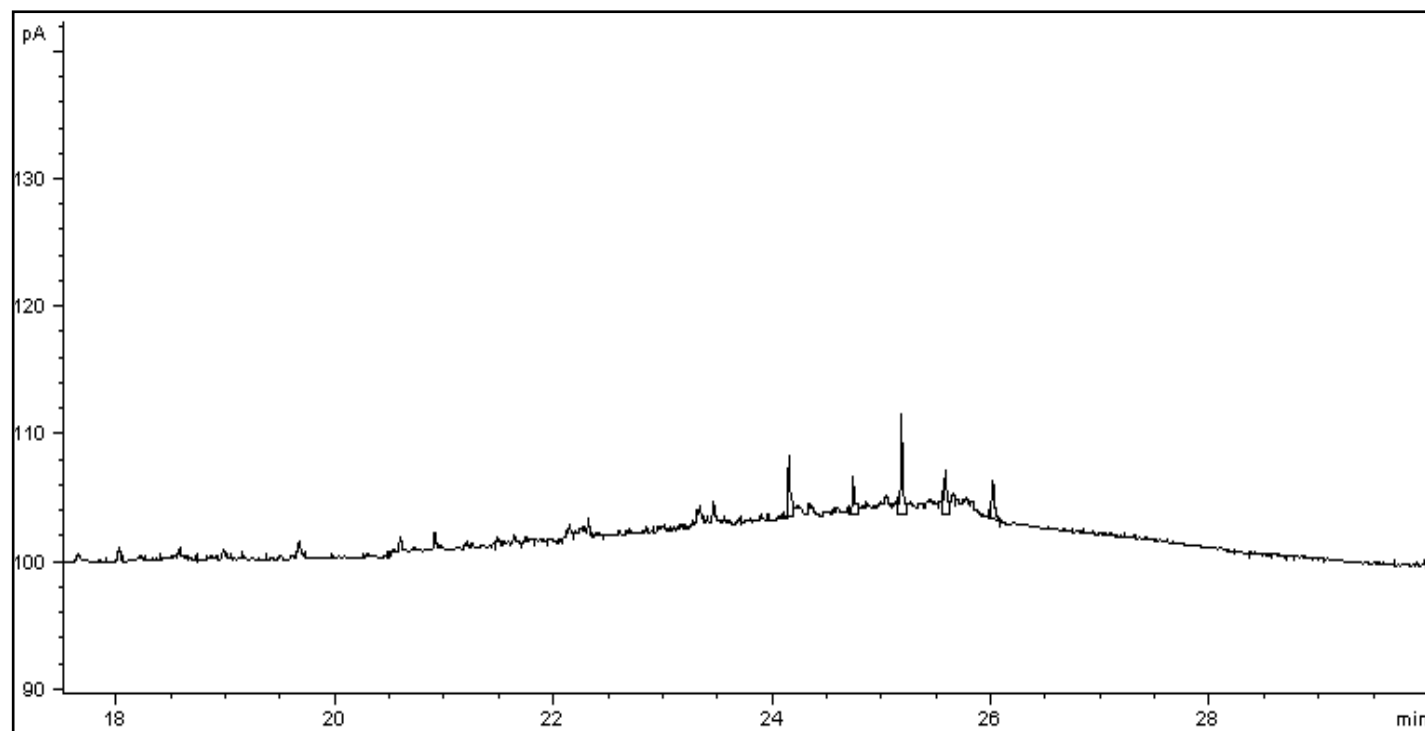


**Figure 4.8:** Gas chromatogram of aliphatic fraction of oil extracted with water at 350°C (17.5-30 min.)

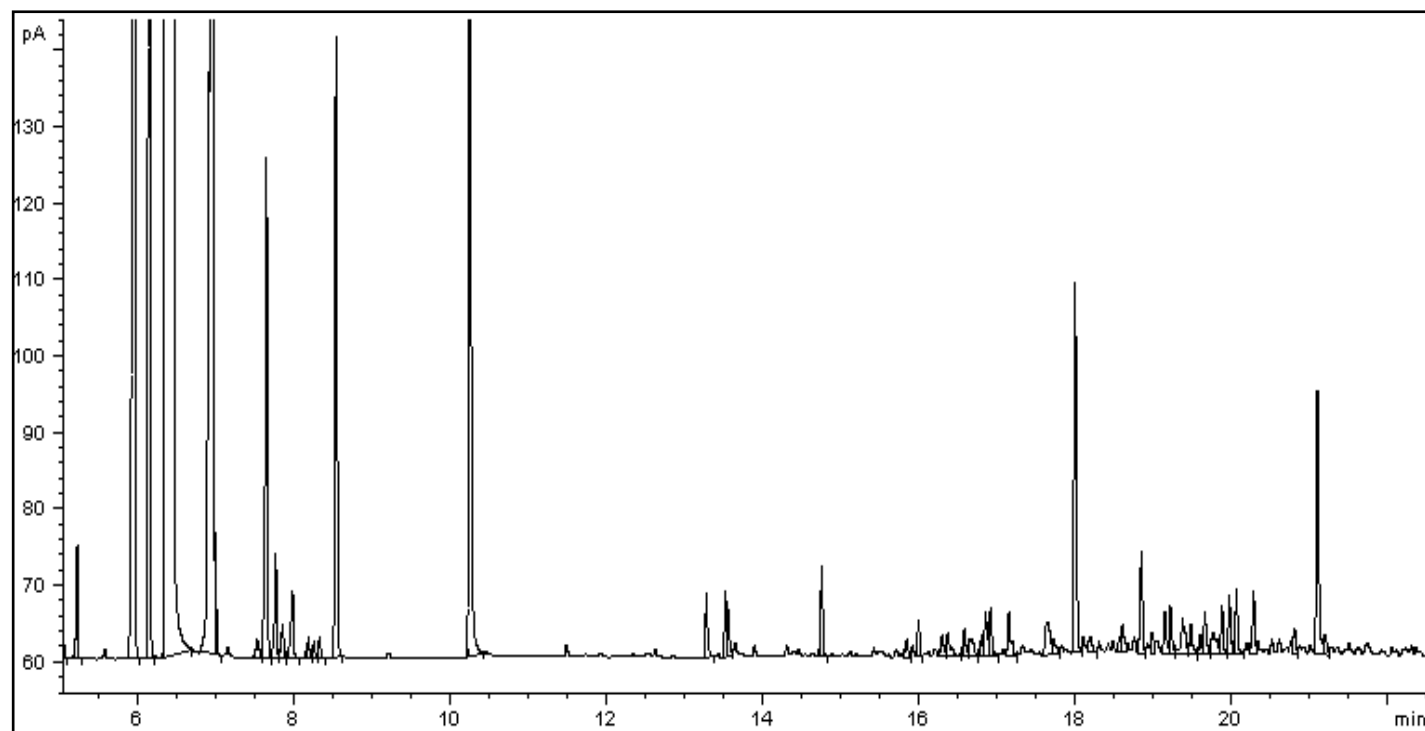


**Figure 4.9:** Gas chromatogram of aliphatic fraction of oil extracted with toluene at 350°C (5-22.5 min.)

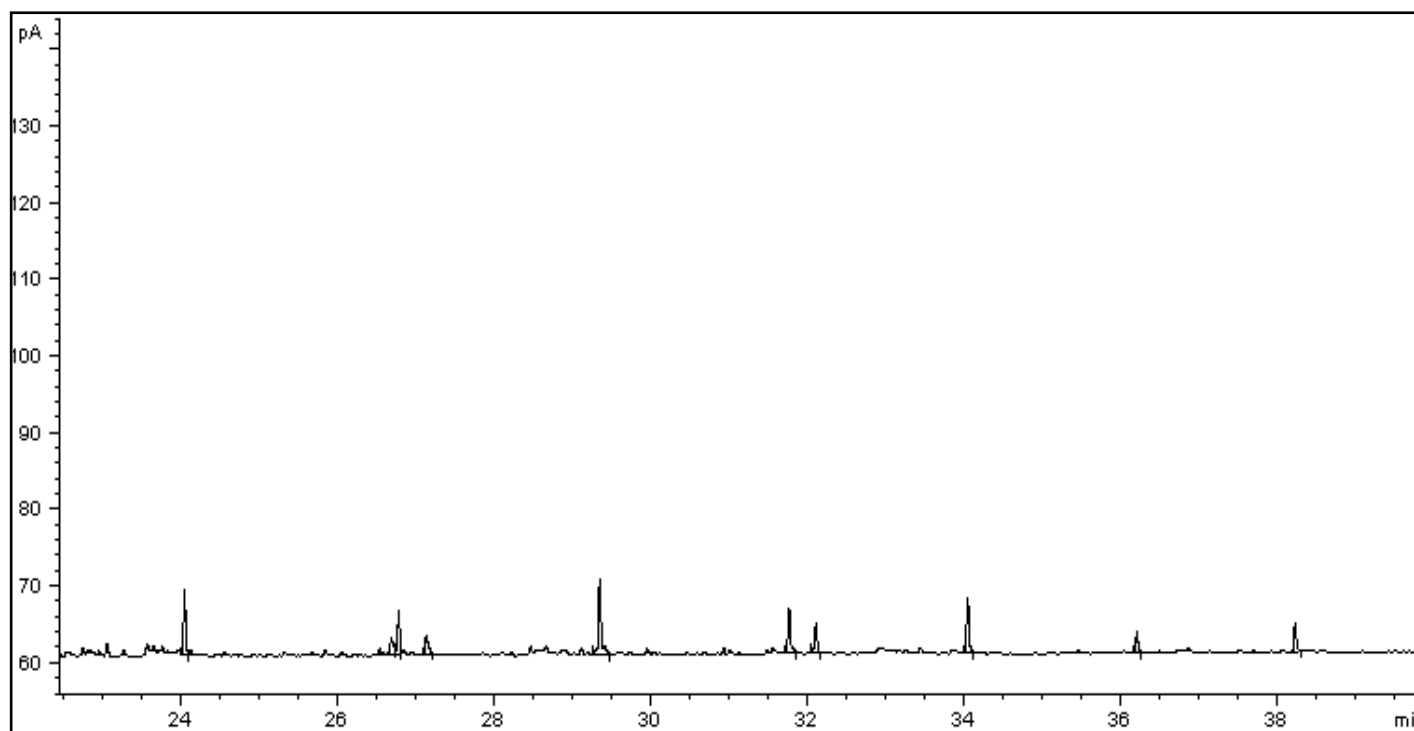


**Figure 4.10:** Gas chromatogram of aliphatic fraction of oil extracted with toluene at 350°C (22.5-40 min.)

## 5. EVALUATION OF RESULTS

### 5.1 Soxhlet Extraction of Activated Sludge

Soxhlet extraction of sewage sludge obtained from Aliaga-petrochemical complex wastewater treatment plant was carried out with different solvents. Total conversion of organic matter is given in Table 5.1. Total conversion of organic matter reached maximum value when the mixture of dichloromethane and methanol was used as solvent. Also, THF and toluene are powerful solvents to dissolve organic matter in activated sludge, thus, toluene was used as a solvent for supercritical extraction experiment and THF was used to wash inside of autoclave after supercritical extraction. Also, all Soxhlet extraction experiments were performed for 8 hours.

High recovery of organic matters was obtained by using solvent having the similar functional groups with the hydrocarbon compounds in the sludge.

**Table 5.1:** Soxhlet extraction of sewage sludge obtained from Aliaga-petrochemical complex wastewater treatment plant

| Solvent                           | Total conversion of organic matter (wt. %) | Dipole Moment of solvent (Debye) | Solubility parameter (cal/cm <sup>3</sup> ) <sup>1/2</sup> | Polarity  |
|-----------------------------------|--------------------------------------------|----------------------------------|------------------------------------------------------------|-----------|
| *Dichloromethane-Methanol mixture | 31.52                                      | 1.65                             | 12.70                                                      | Polar     |
| Acetic acid                       | 31.25                                      | 1.50                             | 10.10                                                      | Polar     |
| THF                               | 30.62                                      | 1.63                             | 9.10                                                       | H-bonding |
| Toluene                           | 29.28                                      | 0.36                             | 8.90                                                       | Polar     |
| o-Xylene                          | 29.23                                      | 0.45                             | 8.85                                                       | Polar     |
| Pyridine                          | 28.15                                      | 2.20                             | 10.61                                                      | H-bonding |
| Dichloromethane                   | 27.67                                      | 1.60                             | 9.93                                                       | Polar     |
| Acetone                           | 26.62                                      | 2.70                             | 9.77                                                       | Polar     |

Table 5.1 continued

|                      |       |      |       |           |
|----------------------|-------|------|-------|-----------|
| Tetraline            | 26.58 | 0.00 | 8.80  | non-polar |
| Isopropanol          | 25.60 | 1.66 | 11.5  | H-bonding |
| Carbon tetrachloride | 25.46 | 0.00 | 8.60  | non-polar |
| Carbon disulphide    | 22.81 | 0.00 | 10.00 | non-polar |
| Cyclohexane          | 23.16 | 0.00 | 8.20  | non-polar |
| Ethanol              | 20.50 | 1.70 | 12.70 | H-bonding |
| n-hexane             | 19.24 | 0.00 | 7.40  | non-polar |
| Methanol             | 18.98 | 1.70 | 14.40 | H-bonding |
| Cyclohexanol         | 13.01 | 1.70 | 11.40 | H-bonding |
| Water                | 7.47  | 1.86 | 23.40 | H-bonding |

\*1/1 volume fraction

## 5.2 Supercritical Fluid Extraction of Activated Sludge

Extraction of petrochemical originated activated sludge samples were carried out by using water and toluene as supercritical fluids. Solvent/solid ratios were selected as 3, 1.5 and 1. In these ratios, amount of solvent was held constant, while amount of sludge was changed. Reaction temperatures were selected as 350°C, 375°C, 400°C, 425°C and 450°C for extraction with water and 300°C, 350°C, 375°C, 400°C, 425°C and 450°C for extraction with toluene. Critical temperature and pressure are 374°C and 220 bar for water and 318°C and 41 bar for toluene, respectively. Lowest selected temperatures for each solvent don't satisfy the supercritical condition. Effect of sub and supercritical conditions on total product yield (gas and extract yield) and distributions of products were examined and optimum reaction conditions were selected for the proper economical and environmental point of view. All reactions were carried out for 1 hour after reaching the reaction temperature.

Initial studies were focused on the effect of solvent/solid ratio and temperature on the product yield of activated sludge, which is extracted with water and toluene, separately. The distribution of gas products evolved from the extraction of activated sludge with water and toluene were examined by changing solvent/solid ratio and temperature. Finally, variation of yield and hydrocarbon distribution of liquid products with temperature was evaluated by analyzing liquid product (hexane soluble) by IR and liquid absorption chromatography.

### 5.2.1 Effect of Solvent/Solid Ratio on Product Yield

Initially, supercritical water and toluene extraction experiments were performed at two different temperatures were selected that to be 400°C and 425°C for all solvent/ solid ratios. The main purpose of this part was determination of optimum solvent/solid ratio. Then, experiments were carried out at optimum solvent/solid ratio by changing temperature from subcritical to supercritical states with water and toluene, separately.

#### 5.2.1.1 Supercritical Water Extraction

Operating conditions for SCWE of activated sludge studies were given in Table 5.2. The total amount of reaction mixture increased by decreasing solvent/solid ratio, so the pressure in batch autoclave increased. Also, pressure was increased by increasing temperature.

**Table 5.2:** Operating conditions of activated sludge for SCWE

| <b>Temperature (°C)</b>          | <b>400</b> |         |       | <b>425</b> |         |       |
|----------------------------------|------------|---------|-------|------------|---------|-------|
| <b>Solvent/Solid Ratio</b>       | 3          | 1.5     | 1     | 3          | 1.5     | 1     |
| <b>Solvent/Solid Ratio (g/g)</b> | 10/3.33    | 10/6.66 | 10/10 | 10/3.33    | 10/6.66 | 10/10 |
| <b>P<sub>max</sub> (bar)</b>     | 220        | 235     | 245   | 230        | 250     | 265   |
| <b>Reaction time (h)</b>         | 1          | 1       | 1     | 1          | 1       | 1     |

Variation of SCWE product yield with solvent/solid ratio at selected two temperatures, which were 400°C and 425°C, was given in Table 5.3. When solvent/solid ratio decreased, extract yield decreased and gas product yield increased while amount of residue remains nearly constant for the study at 400°C (Figure 5.1). Same decreasing trend of extract and increasing trend of gas products were also observed for the experiments at 400°C and 425°C (Figure 5.1 and 5.2). Because, at higher solvent/solid ratios (as amount of solvent was higher relative to solid), solvent has more capability to dissolve extractable matter in solid by diffusing into porous. When solvent/solid ratios were 3, 1.5 and 1, extract yields at 400°C were 49.81 wt.%, 48.46 wt.% and 43.00 wt.% and extract yields at 425°C were 46.19 wt.%, 45.06 wt.% and 44.40 wt.%, respectively. As the temperature increases extract yield

decreases, because of conversion of liquid products into gas products. It is known that, at higher temperatures, the secondary reactions take place and the liquid will be converted into gas. This hypothesis seems reasonable because the gas at 400°C was 18.70 wt.% and at 425°C was 19.10 wt.%.

**Table 5.3:** Variation of product yield for SCWE with solvent/solid ratio at selected temperatures

| Solvent/Solid<br>ratio | Temperature (°C)  |                   |               |                   |                   |               |
|------------------------|-------------------|-------------------|---------------|-------------------|-------------------|---------------|
|                        | 400               |                   |               | 425               |                   |               |
|                        | Residue<br>(wt.%) | Extract<br>(wt.%) | Gas<br>(wt.%) | Residue<br>(wt.%) | Extract<br>(wt.%) | Gas<br>(wt.%) |
| 3                      | 38.19             | 49.81             | 12.00         | 36.96             | 46.19             | 16.85         |
| 1.5                    | 36.68             | 48.46             | 14.86         | 37.78             | 45.06             | 17.16         |
| 1                      | 38.30             | 43.00             | 18.70         | 36.50             | 44.40             | 19.10         |

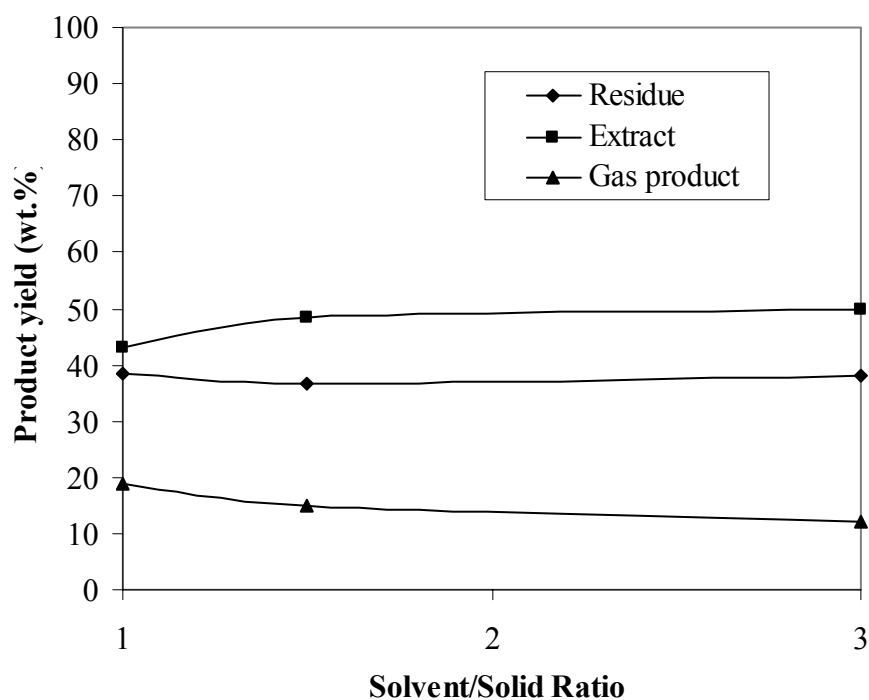


**Figure 5.1:** Variation of SCWE product yield with solvent/solid ratio at 400°C

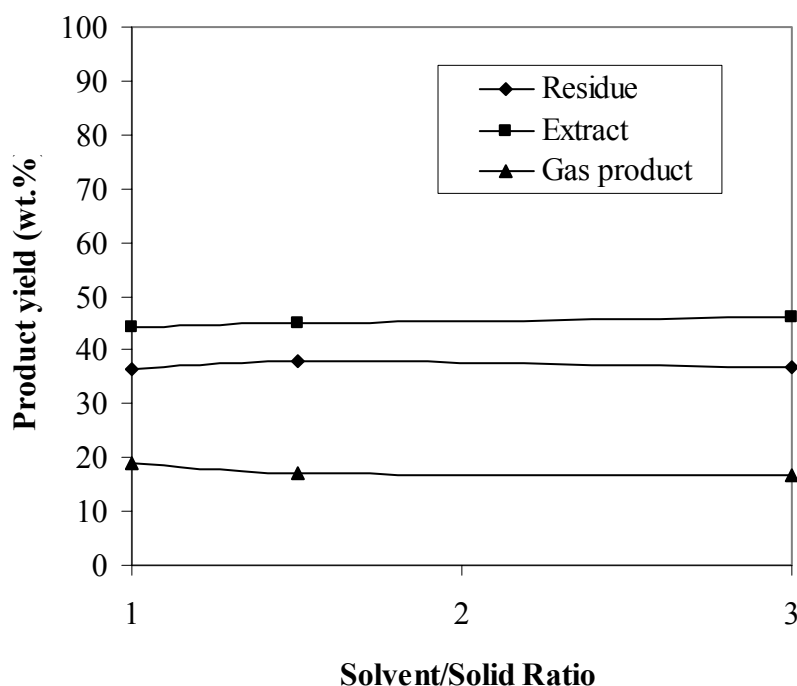


**Figure 5.2:** Variation of SCWE product yield with solvent/solid ratio at 425°C

**Table 5.4:** Variation of total product yield and total conversion of organic matter (TCOM) with solvent/solid ratio for SCWE at selected temperatures

| Solvent/Solid<br>ratio | Temperature (°C)       |                 |                        |                 |
|------------------------|------------------------|-----------------|------------------------|-----------------|
|                        | 400                    |                 | 425                    |                 |
|                        | Total Yield<br>(wt. %) | TCOM<br>(wt. %) | Total Yield<br>(wt. %) | TCOM<br>(wt. %) |
| 3                      | 61.81                  | 81.52           | 63.04                  | 83.15           |
| 1.5                    | 63.32                  | 83.51           | 62.22                  | 82.06           |
| 1                      | 61.70                  | 81.38           | 63.50                  | 83.75           |

Also, total product yields (extract and gas yields) must be considered for selection of optimum solvent/solid ratio. As shown in Table 5.4, total product yields were very close to each other. However, cost of solvent removal from extract and environmental effect of hazardous solvents (except water) were stringent constraints for selection. When the all of these results were evaluated together, optimum solvent/solid ratio was taken to be 1 for SCWE of sludge.

### 5.2.1.2 Supercritical Toluene Extraction

Toluene is also one of the most commonly examined solvents for supercritical extraction applied to carbonaceous materials in order to obtain liquid fuels.

Operating conditions for SCTE of activated sludge were given in Table 5.5. Same operating conditions were selected with SCWE, to be able to compare the results.

**Table 5.5:** Operating conditions of activated sludge for SCTE

| Temperature(°C)           | 400     |         |       | 425     |         |       |
|---------------------------|---------|---------|-------|---------|---------|-------|
| Solvent/Solid Ratio       | 3       | 1.5     | 1     | 3       | 1.5     | 1     |
| Solvent/Solid Ratio (g/g) | 10/3.33 | 10/6.66 | 10/10 | 10/3.33 | 10/6.66 | 10/10 |
| P <sub>max</sub> (bar)    | 85      | 120     | 145   | 115     | 150     | 190   |
| Reaction time (h)         | 1       | 1       | 1     | 1       | 1       | 1     |

Variation of product yield with solvent/solid ratio for SCTE at selected temperatures was tabulated in Table 5.6. When solvent/solid ratios were 3, 1.5 and 1, extract yields at 400°C were 41.88 wt. %, 37.88 wt. % and 36.50 wt. %, and at 425°C were found to be 38.46 wt. %, 32.34 wt. % and 30.32 wt.%, respectively. With the similar results of SCWE of activated sludge, gas product yields increased by decreasing solvent/solid ratio and/or increasing temperature. If temperature was increased from 400°C to 425°C by keeping solvent/solid ratio constant, it's realized that liquid products converted to gas products, by the way, solid part was converted to liquid.

**Table 5.6:** Variation of product yield with solvent/solid ratio for SCTE at selected temperatures

| Solvent/Solid ratio | Temperature (°C) |                |            |                |                |            |
|---------------------|------------------|----------------|------------|----------------|----------------|------------|
|                     | 400              |                |            | 425            |                |            |
|                     | Residue (wt.%)   | Extract (wt.%) | Gas (wt.%) | Residue (wt.%) | Extract (wt.%) | Gas (wt.%) |
| <b>3</b>            | 45.32            | 41.88          | 12.80      | 43.74          | 38.46          | 17.80      |
| <b>1.5</b>          | 45.92            | 37.88          | 16.20      | 45.46          | 32.34          | 22.20      |
| <b>1</b>            | 44.20            | 36.50          | 19.30      | 42.21          | 30.32          | 27.47      |

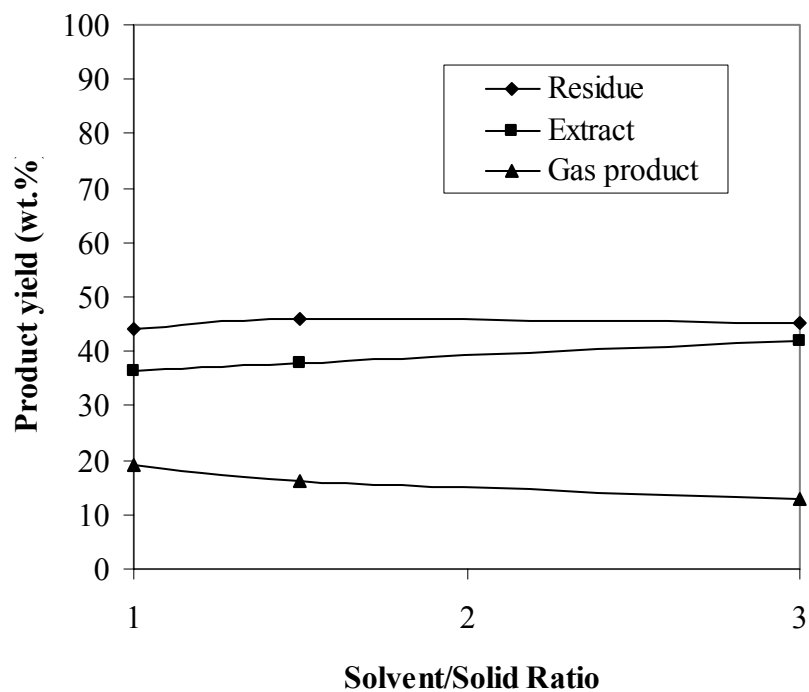


**Figure 5.3:** Variation of SCTE product yield with solvent/solid ratio at 400°C

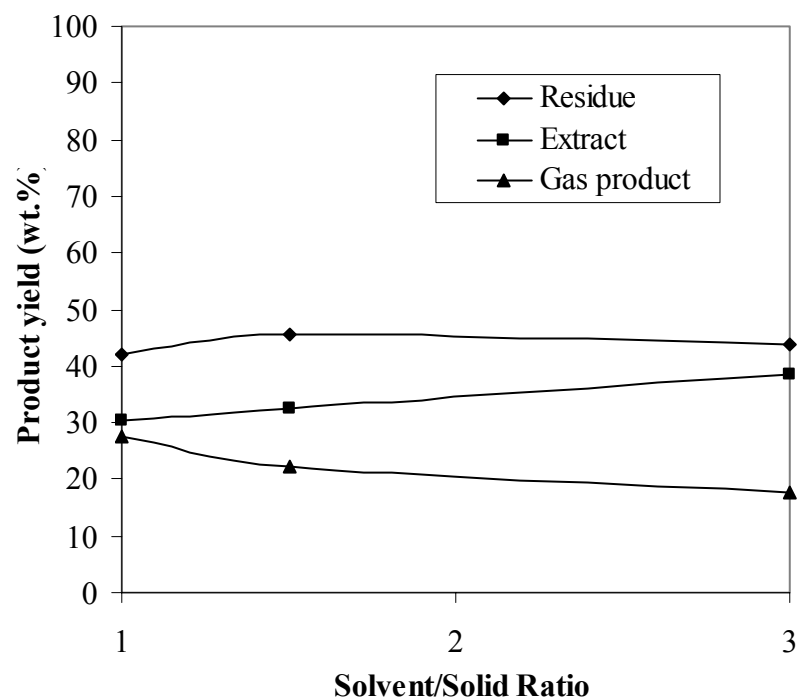


**Figure 5.4:** Variation of SCTE product yield with solvent/solid ratio at 425°C

**Table 5.7:** Variation of total product yield and total conversion of organic matter (TCOM) with solvent/solid ratio for SCTE at selected temperatures

| Solvent/Solid<br>ratio | Temperature (°C)       |                 |                        |                 |
|------------------------|------------------------|-----------------|------------------------|-----------------|
|                        | 400                    |                 | 425                    |                 |
|                        | Total Yield<br>(wt. %) | TCOM<br>(wt. %) | Total Yield<br>(wt. %) | TCOM<br>(wt. %) |
| <b>3</b>               | 54.68                  | 72.12           | 56.26                  | 74.20           |
| <b>1.5</b>             | 54.08                  | 71.33           | 54.54                  | 71.93           |
| <b>1</b>               | 55.80                  | 73.59           | 57.79                  | 76.22           |

Extract and total product yields in SCTE were lower, but gas product yields in SCTE were higher than SCWE at the same conditions (Table 5.4 and Table 5.7). According to these results, water should be more suitable for extraction of products from activated sludge to be able to reach higher yields.

Because of small difference in yields, solvent/solid ratio was selected to be 1 because of the small difference in yields. It was meaningless to spent high amount of solvent to obtain nearly same conversion values. Also, total product yields were higher when solvent/solid ratio was 1. At this selected ratio, total product yields were 55.80 wt.% and 57.79 wt.% at 400°C and 425°C, respectively.

As a result, optimum solvent/solid ratio was 1 for extraction of activated sewage sludge with water and toluene, separately.

### 5.2.2 Effect of Temperature on Product Yield

After selection of optimum solvent/solid ratio to be 1, effect of temperature on product yield was investigated to obtain optimum reaction temperature. Experiments were also performed by using water and toluene as solvents. But, only product yields were not enough to be able to decide optimum reaction temperature, also extract and gas product distribution must be evaluated in detail.

### 5.2.2.1 Supercritical Water Extraction

Extraction of activated sludge with water was performed by taking solvent/solid ratio as 1 and varying temperature from 350°C and 450°C increasing by 25°C. Lowest selected temperature that was 350°C, satisfies subcritical condition for water extraction. Reaction was carried out for 1 h, after reaching reaction temperature. Operating conditions of SCWE of activated sludge were given in Table 5.8.

**Table 5.8:** Operating conditions of activated sludge for SCWE

|                                  |       |       |       |       |       |
|----------------------------------|-------|-------|-------|-------|-------|
| <b>Temperature (°C)</b>          | *350  | 375   | 400   | 425   | 450   |
| <b>Solvent/Solid Ratio</b>       | 1     | 1     | 1     | 1     | 1     |
| <b>Solvent/Solid Ratio (g/g)</b> | 10/10 | 10/10 | 10/10 | 10/10 | 10/10 |
| <b>P<sub>max</sub>(bar)</b>      | 215   | 230   | 245   | 265   | 300   |
| <b>Reaction time (h)</b>         | 1     | 1     | 1     | 1     | 1     |

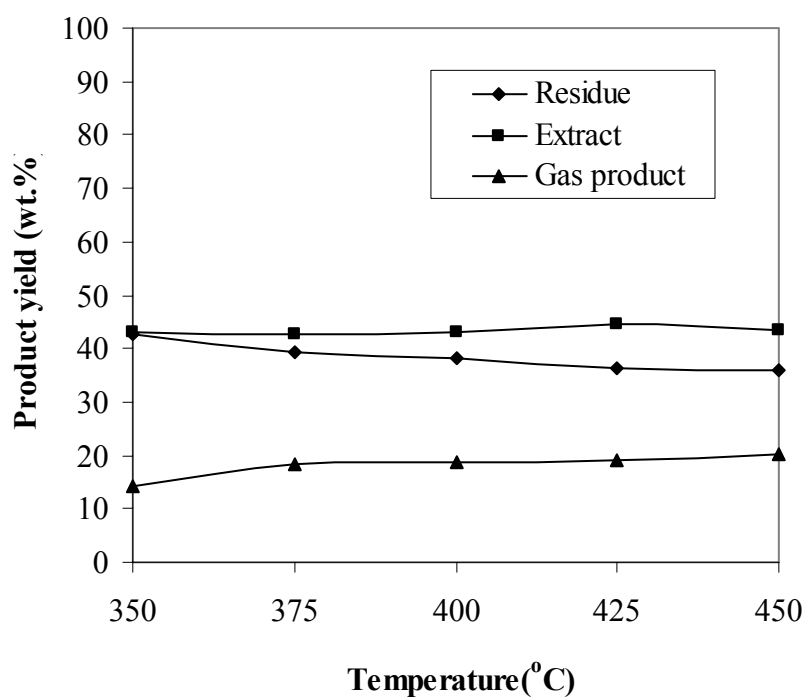
\*Subcritical condition

Variation of SCWE product yield with temperature was outlined in Table 5.9 and Figure 5.5, when solvent/solid ratio was 1. Gas product yield increased from 14.30 wt.% to 20.40 wt.% by increasing temperature from 350°C to 450°C. Also, amount of residue decreased by increasing temperature. It can be explained by conversion of activated sludge into liquid and gas products increases by increasing temperature. But, conversion of activated sludge ratios into extracts and gas products change with temperature.

Total product yield (extract and gas) increased by increasing temperature because of thermal cracking of high molecular weight species into smaller ones. Also, it is expected that, at higher temperatures, secondary reactions take place and extract will be degraded. Extract yield had maximum value at 425°C.

**Table 5.9:** Variation of product yield with temperature for SCWE (Solvent/Solid Ratio: 1)

| Temperature<br>(°C) | 350   | 375   | 400   | 425   | 450   |
|---------------------|-------|-------|-------|-------|-------|
| Product Yield(%)    |       |       |       |       |       |
| <b>Residue</b>      | 42.70 | 39.28 | 38.30 | 36.50 | 36.02 |
| <b>Extract</b>      | 43.00 | 42.52 | 43.00 | 44.40 | 43.58 |
| <b>Gas</b>          | 14.30 | 18.20 | 18.70 | 19.10 | 20.40 |

**Figure 5.5:** Variation of SCWE product yield with temperature (Solvent/Solid Ratio: 1)

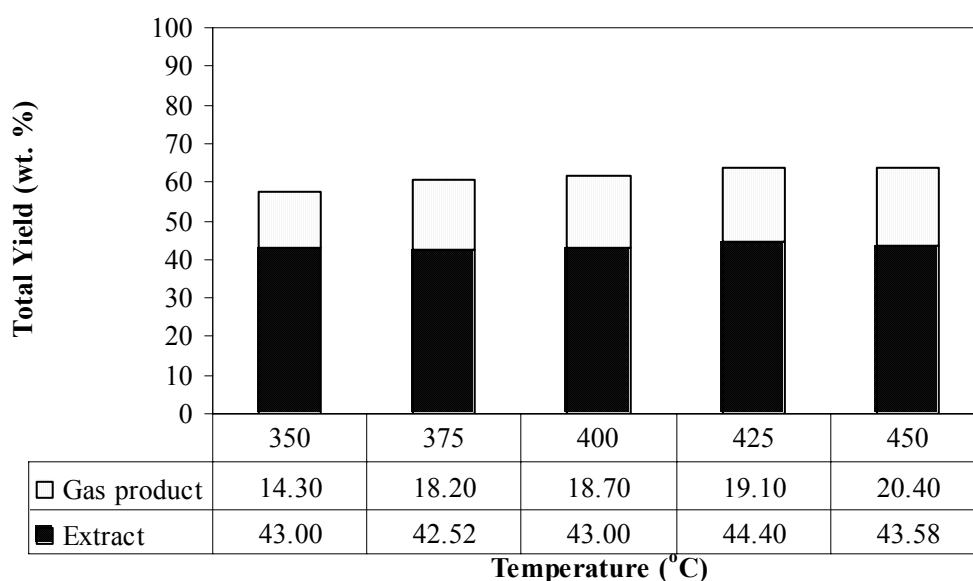


**Figure 5.6:** Variation of SCWE total product yield with temperature (Solvent/Solid Ratio: 1)

### 5.2.2.2 Supercritical Toluene Extraction

Extraction of activated sludge with toluene was performed by taking solvent/solid ratio to be 1 and varying temperatures from 300°C and 450°C. Lowest selected temperature that was 300°C satisfies subcritical condition for toluene extraction. Reaction was carried out for 1 h, after reaching reaction temperature. Operating conditions of SCTE of activated sludge were given in Table 5.10.

**Table 5.10:** Operating conditions of activated sludge for SCTE

| Temperature(°C)           | *300  | 350   | 375   | 400   | 425   | 450   |
|---------------------------|-------|-------|-------|-------|-------|-------|
| P <sub>max</sub> (bar)    | 85    | 115   | 140   | 145   | 190   | 200   |
| Solvent/Solid Ratio (g/g) | 10/10 | 10/10 | 10/10 | 10/10 | 10/10 | 10/10 |
| Reaction time (h)         | 1     | 1     | 1     | 1     | 1     | 1     |

\*Subcritical condition

Variation of SCTE product yield with temperature was outlined in Table 5.11 and Figure 5.7, when solvent/solid ratio was 1. Gas product yield increased from 8.90 wt.% to 30.20 wt.% by increasing temperature from 300°C to 450°C. Also, amount of residue

decreased by increasing temperature. Extract yield decreased from 44.97 wt.% to 28.46 wt.% by increasing temperature. Total product yield increased as temperature increased, because conversion of extract into gas products increased. Extract yield has reached maximum value at 300°C, which is subcritical condition.

**Table 5.11:** Variation of product yield with temperature for SCTE (Solvent/Solid Ratio: 1)

| Temperature (°C)<br>Product Yield (%) | 300   | 350   | 375   | 400   | 425   | 450   |
|---------------------------------------|-------|-------|-------|-------|-------|-------|
| Residue                               | 46.13 | 44.68 | 44.31 | 44.20 | 42.21 | 41.34 |
| Extract                               | 44.97 | 41.92 | 37.89 | 36.50 | 30.33 | 28.46 |
| Gas                                   | 8.90  | 13.40 | 17.80 | 19.30 | 27.47 | 30.20 |

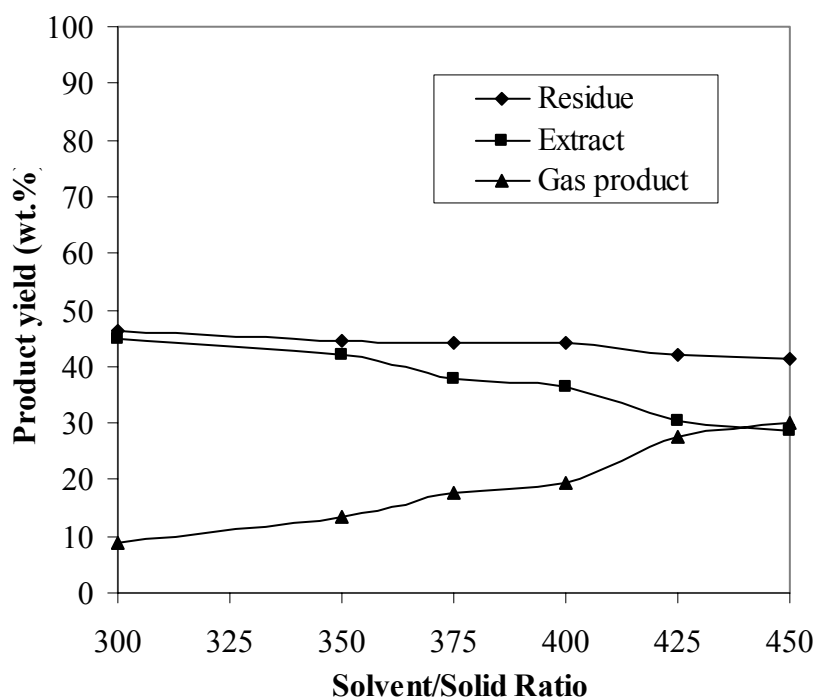


**Figure 5.7:** Variation of SCTE product yield with temperature (Solvent/Solid Ratio: 1)

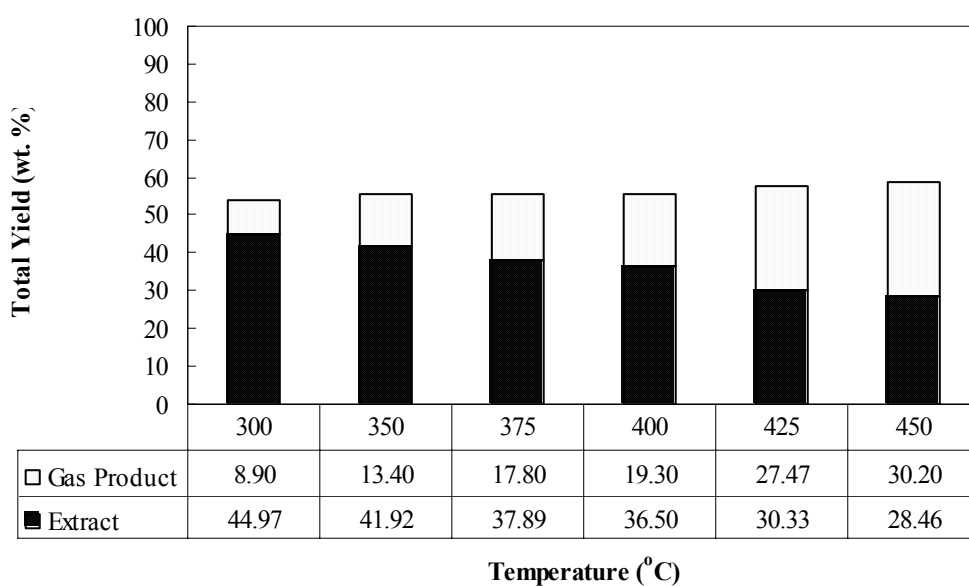


**Figure 5.8:** Variation of SCTE total product yield with temperature (Solvent/Solid Ratio: 1)

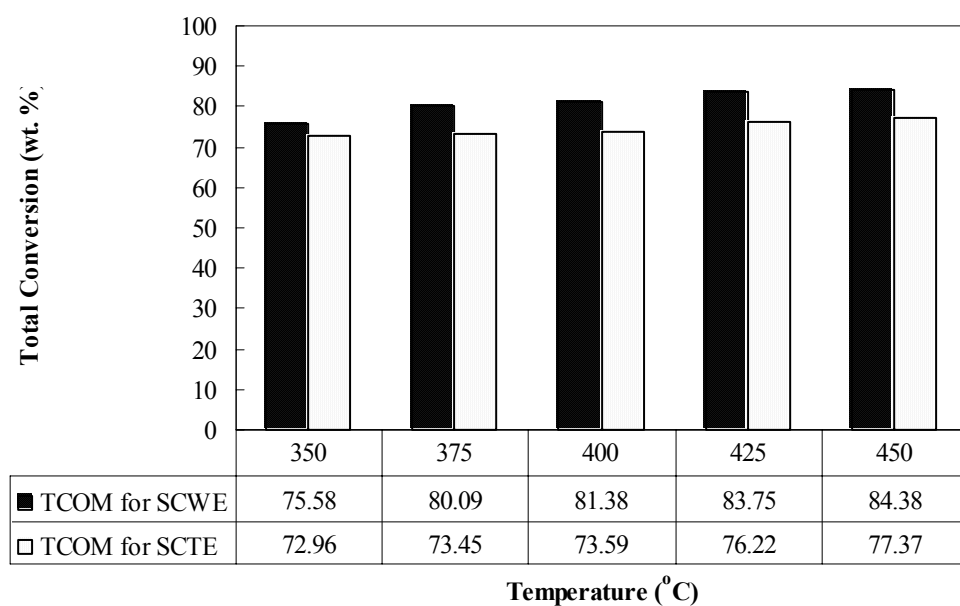


**Figure 5.9:** Variation of total conversion of organic matter in SCWE and SCTE of activated sludge with temperature

If total product yield and total conversion of organic matter for SCWE and SCTE were compared at every temperature, these values were higher in SCWE than SCTE. (Figure 5.9)

### 5.2.3 Effect of solvent/solid ratio on gas product distribution

In this section, effect of solvent/solid ratio on gas product distribution at 400°C and 425°C were examined for SCWE and SCTE of activated sludge, separately. In both of extraction processes, gas product distributions were given in volume and weight percentages. Because, results evaluated only by volume percentages could be mislead. Also, weight percentages must be taken into consideration during evaluation. Difference in densities of gas products causes variation in volume and weight percentages.

#### 5.2.3.1 Supercritical Water Extraction

Effect of solvent/solid ratio on gas product distribution at 400°C and 425°C were examined for SCWE of activated sludge. Solvent/solid ratios were selected as 3, 1.5 and 1. Major products were CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>.

Variation of gas product distribution of SCWE of activated sludge at 400°C was given by volume in Table 5.12 and Figure 5.10. According to these results, amount of CO<sub>2</sub> increased, CH<sub>4</sub> decreased slightly and H<sub>2</sub> decreased by volume, when the solvent/solid ratio increased.

Variation of gas product distribution of SCWE of activated sludge at 400°C was given by weight in Table 5.13 and Figure 5.11. Amount of CO<sub>2</sub> decreased, CH<sub>4</sub> and H<sub>2</sub> decreased slightly by weight, when the solvent/solid ratio increased. The difference of tendencies in amount of CO<sub>2</sub> by volume and weight can be explained by the different density of gas products.

**Table 5.12:** Variation of gas product distribution at 400°C for SCWE (by volume percentage)

| <b>Solvent/Solid Ratio</b><br><b>Components</b> | <b>1</b> | <b>1.5</b> | <b>3</b> |
|-------------------------------------------------|----------|------------|----------|
| <b>CH<sub>4</sub></b>                           | 14.11    | 13.21      | 13.92    |
| <b>CO<sub>2</sub></b>                           | 40.69    | 44.67      | 42.12    |
| <b>C<sub>2</sub></b>                            | 6.46     | 7.39       | 7.71     |
| <b>C<sub>3</sub></b>                            | 6.36     | 7.69       | 8.48     |
| <b>C<sub>4</sub></b>                            | 3.76     | 4.65       | 5.81     |
| <b>C<sub>5</sub></b>                            | 1.22     | 1.81       | 2.77     |
| <b>C<sub>6</sub><sup>+</sup></b>                | 0.64     | 0.96       | 1.40     |
| <b>H<sub>2</sub></b>                            | 26.75    | 19.62      | 17.79    |

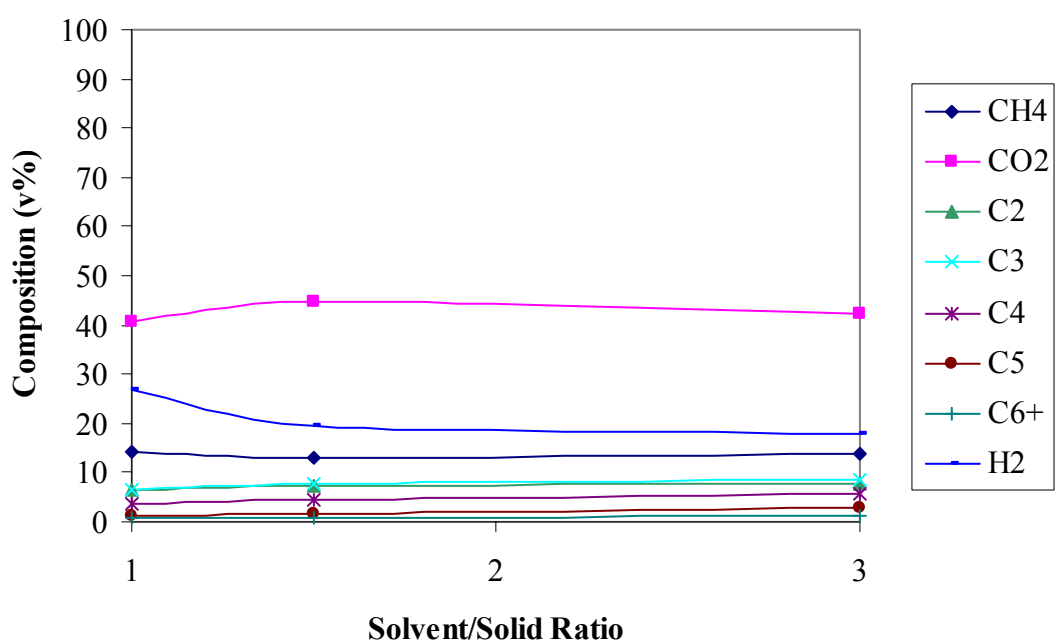
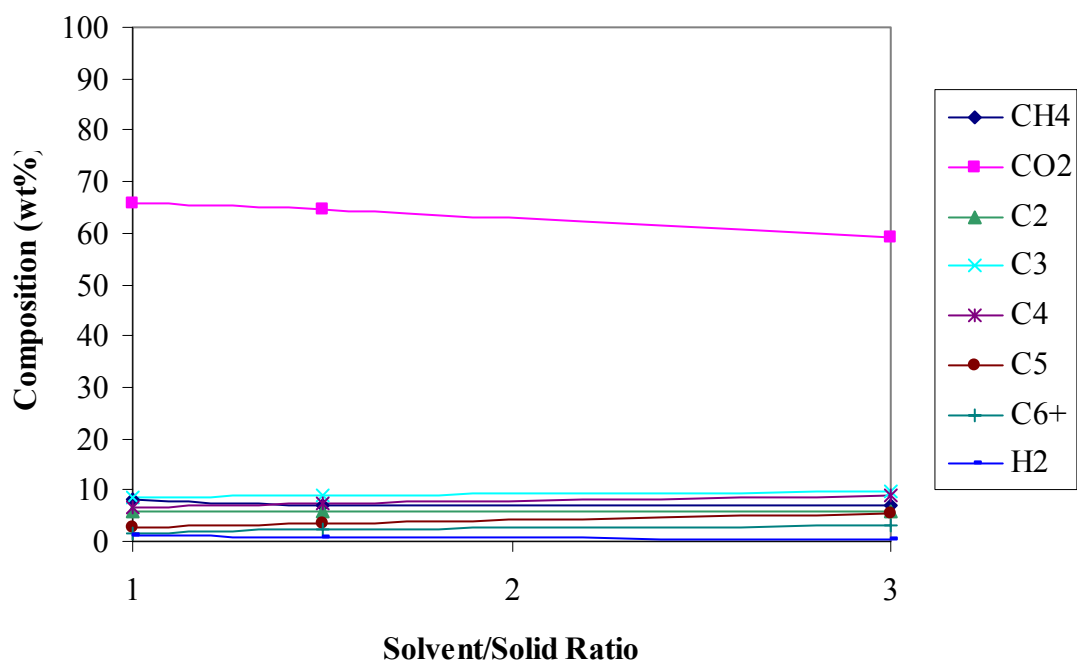
**Figure 5.10:** Variation of gas product distribution of SCWE at 400°C (by volume percentage)

**Table 5.13:** Variation of gas product distribution at 400°C for SCWE (by weight percentage)

| <b>Solvent/Solid Ratio</b><br><b>Components</b> | <b>1</b> | <b>1.5</b> | <b>3</b> |
|-------------------------------------------------|----------|------------|----------|
| <b>CH<sub>4</sub></b>                           | 8.29     | 6.93       | 7.11     |
| <b>CO<sub>2</sub></b>                           | 65.71    | 64.41      | 59.22    |
| <b>C<sub>2</sub></b>                            | 5.69     | 5.81       | 5.91     |
| <b>C<sub>3</sub></b>                            | 8.40     | 9.07       | 9.75     |
| <b>C<sub>4</sub></b>                            | 6.62     | 7.31       | 8.91     |
| <b>C<sub>5</sub></b>                            | 2.69     | 3.56       | 5.31     |
| <b>C<sub>6</sub><sup>+</sup></b>                | 1.69     | 2.27       | 3.21     |
| <b>H<sub>2</sub></b>                            | 0.98     | 0.64       | 0.57     |

**Figure 5.11:** Variation of gas product distribution of SCWE at 400°C (by weight percentage)

Variation of gas product distribution of SCWE of activated sludge at 425°C was given by volume in Table 5.14 and Figure 5.12. According to these results, amount of CO<sub>2</sub> decreased, CH<sub>4</sub> increased slightly and H<sub>2</sub> decreased by volume, when the solvent/solid ratio increased.

Variation of gas product distribution of SCWE of activated sludge at 425°C was given by weight in Table 5.15 and Figure 5.13. When the solvent/solid ratio increased, the amount of CO<sub>2</sub> decreased, CH<sub>4</sub> and H<sub>2</sub> were slightly decreased by weight. The difference of tendencies in amount of CH<sub>4</sub> by volume and weight can be explained by the different density of gas products.

Effect of solvent/solid ratio on gas product distribution was examined at two different temperatures to make results definite. If the results were generalized, there was a decreasing tendency in both volume and weight percentages of CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> by increasing solvent/solid ratio. These changes could be explained by increasing amount of the C<sub>2</sub>-C<sub>6+</sub> products.

Also, comparison of gas product distributions between two temperatures can be made by observing changes. For example, volume percentages of CO<sub>2</sub> decreases, CH<sub>4</sub> and H<sub>2</sub> increases at every solvent/solid ratio by increasing temperature. (Table 5.14 and 5.15)

**Table 5.14:** Variation of gas product distribution at 425°C for SCWE (by volume percentage)

| <b>Solvent/Solid Ratio</b><br><b>Components</b> | <b>1</b> | <b>1.5</b> | <b>3</b> |
|-------------------------------------------------|----------|------------|----------|
| <b>CH<sub>4</sub></b>                           | 18.79    | 16.46      | 19.77    |
| <b>CO<sub>2</sub></b>                           | 36.83    | 28.85      | 26.43    |
| <b>C<sub>2</sub></b>                            | 7.94     | 9.29       | 11.17    |
| <b>C<sub>3</sub></b>                            | 3.72     | 7.82       | 10.49    |
| <b>C<sub>4</sub></b>                            | 2.81     | 4.22       | 6.80     |
| <b>C<sub>5</sub></b>                            | 1.20     | 1.43       | 3.18     |
| <b>C<sub>6+</sub></b>                           | 0.21     | 0.29       | 1.37     |
| <b>H<sub>2</sub></b>                            | 28.51    | 31.65      | 20.79    |

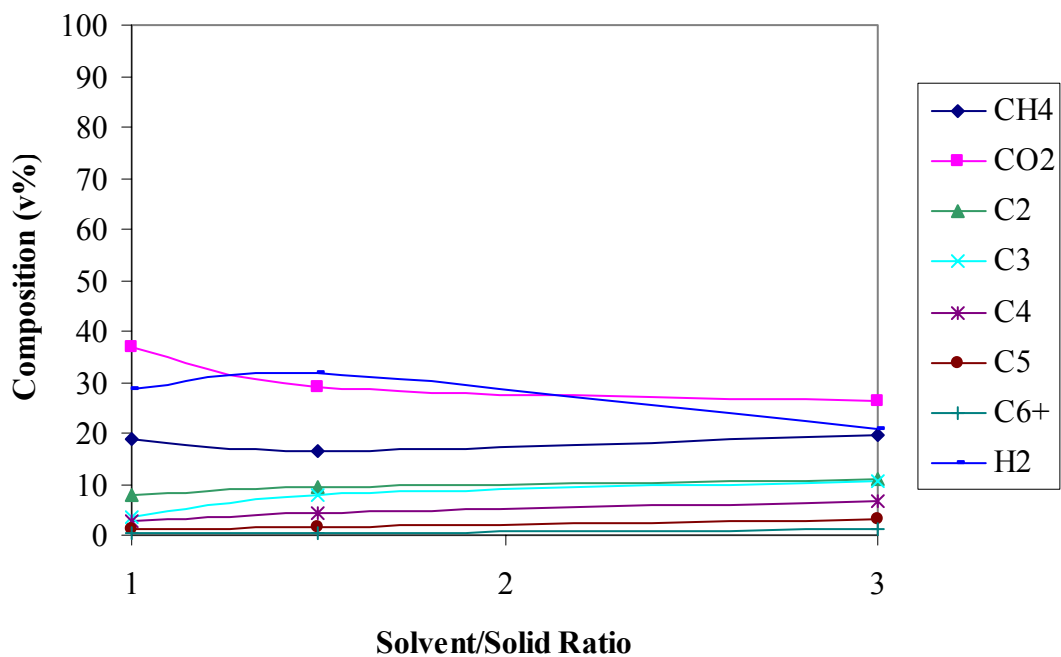


**Figure 5.12:** Variation of gas product distribution of SCWE at 425°C (by volume percentage)

**Table 5.15:** Variation of gas product distribution at 425°C for SCWE (by weight percentage)

| <b>Solvent/Solid Ratio</b><br><b>Components</b> | <b>1</b> | <b>1.5</b> | <b>3</b> |
|-------------------------------------------------|----------|------------|----------|
| <b>CH<sub>4</sub></b>                           | 12.06    | 11.07      | 11.45    |
| <b>CO<sub>2</sub></b>                           | 64.98    | 53.40      | 42.11    |
| <b>C<sub>2</sub></b>                            | 7.64     | 9.37       | 9.71     |
| <b>C<sub>3</sub></b>                            | 5.36     | 11.84      | 13.67    |
| <b>C<sub>4</sub></b>                            | 5.40     | 8.51       | 11.81    |
| <b>C<sub>5</sub></b>                            | 2.88     | 3.60       | 6.92     |
| <b>C<sub>6</sub><sup>+</sup></b>                | 0.60     | 0.87       | 3.57     |
| <b>H<sub>2</sub></b>                            | 1.14     | 1.33       | 0.75     |

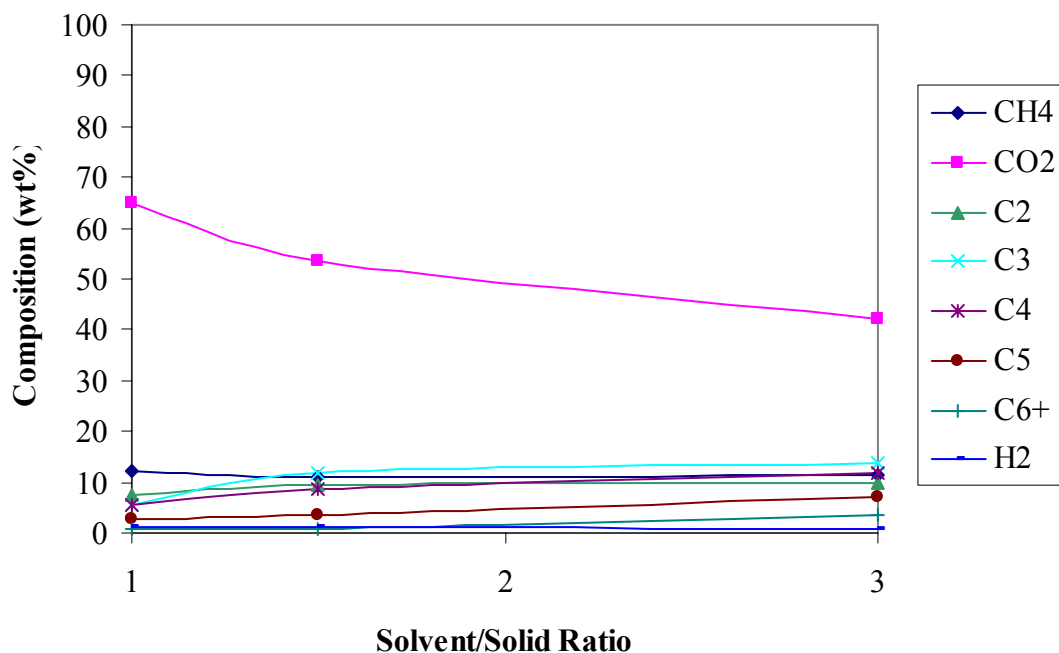


**Figure 5.13:** Variation of gas product distribution of SCWE at 425°C (by weight percentage)

### 5.2.3.2 Supercritical Toluene Extraction

Effect of solvent/solid ratio on gas product distribution at 400°C and 425°C were examined for SCTE of activated sludge. Solvent/solid ratios were selected as 3, 1.5 and 1. Major products were CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub> and C<sub>2</sub>.

Variation of gas product distribution of SCTE of activated sludge at 400°C was given by volume in Table 5.16 and Figure 5.14. According to these results, when the solvent/solid ratio increased, the amount of CH<sub>4</sub> decreases, CO<sub>2</sub> and H<sub>2</sub> increases, C<sub>2</sub> decreases by volume.

Variation of gas product distribution of SCWE of activated sludge at 400°C was given by weight in Table 5.17 and Figure 5.15. When the solvent/solid ratio increased, the amount of CH<sub>4</sub> decreases, CO<sub>2</sub> increases, H<sub>2</sub> increases slightly and C<sub>2</sub> decreases by weight.

There were not any different tendency of product distribution observed by comparing volume and weight percentages. By the way, SCTE at 425°C must be examined to obtain definite results.

**Table 5.16:** Variation of gas product distribution at 400°C for SCTE (by volume percentage)

| <b>Solvent/Solid Ratio</b><br><b>Components</b> | <b>1</b> | <b>1.5</b> | <b>3</b> |
|-------------------------------------------------|----------|------------|----------|
| <b>CH<sub>4</sub></b>                           | 38.74    | 29.42      | 34.88    |
| <b>CO<sub>2</sub></b>                           | 27.90    | 31.15      | 30.41    |
| <b>C<sub>2</sub></b>                            | 11.10    | 11.90      | 10.82    |
| <b>C<sub>3</sub></b>                            | 6.01     | 5.54       | 4.85     |
| <b>C<sub>4</sub></b>                            | 2.00     | 1.40       | 1.34     |
| <b>C<sub>5</sub></b>                            | 0.51     | 0.30       | 0.28     |
| <b>C<sub>6</sub><sup>+</sup></b>                | 0.14     | 0.44       | 0.55     |
| <b>H<sub>2</sub></b>                            | 13.60    | 19.85      | 16.88    |

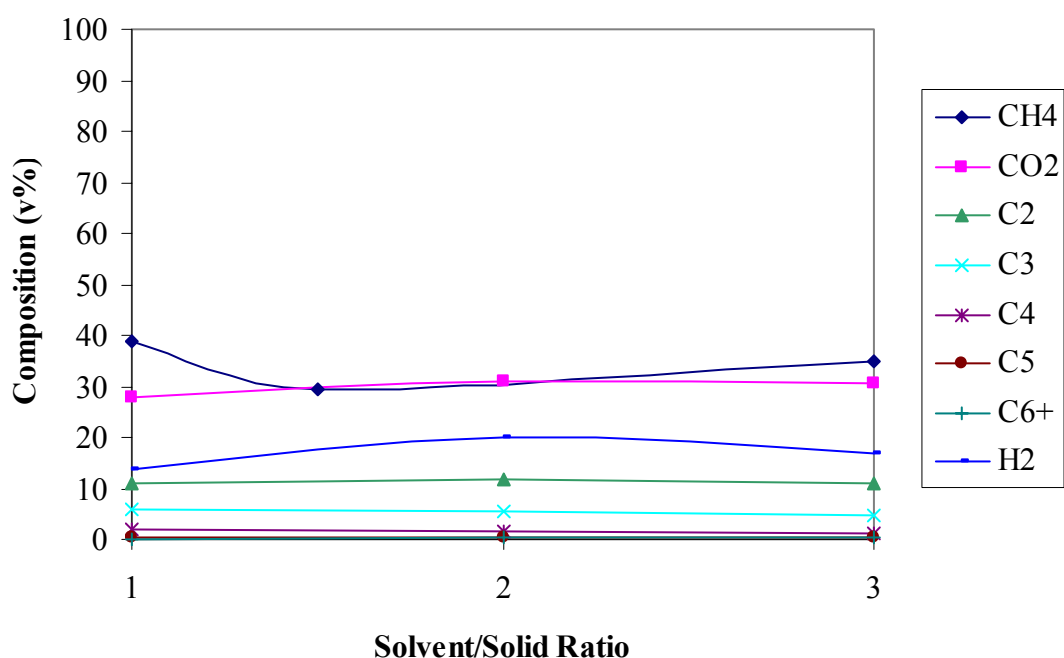
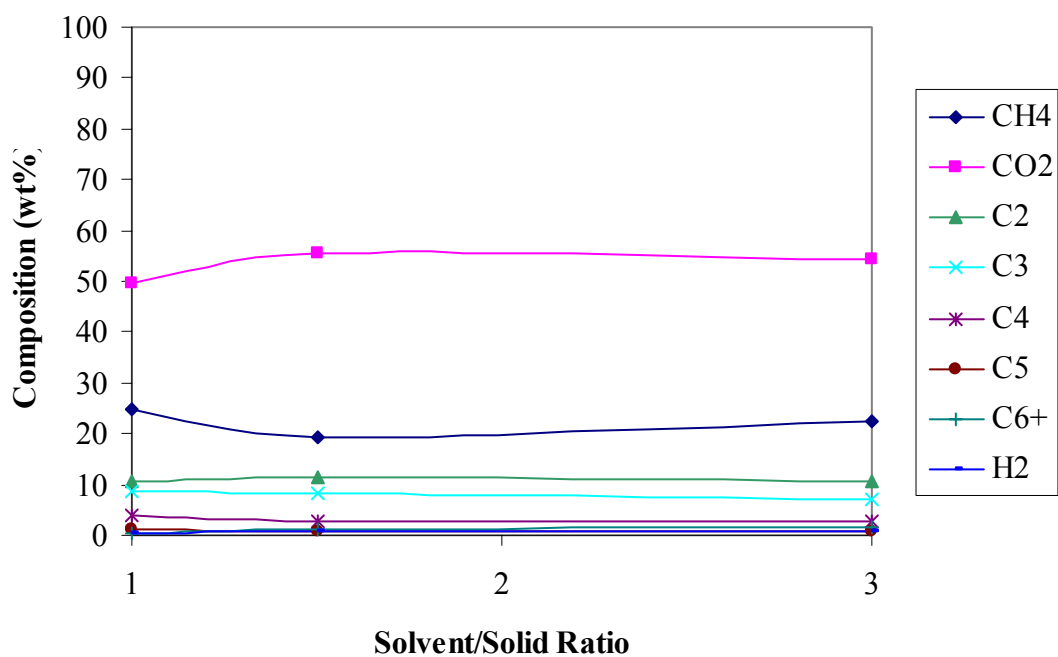


**Figure 5.14:** Variation of gas product distribution of SCTE at 400°C (by volume percentage)

**Table 5.17:** Variation of gas product distribution at 400°C for SCTE (by weight percentage)

| <b>Solvent/Solid Ratio</b><br><b>Components</b> | <b>1</b> | <b>1.5</b> | <b>3</b> |
|-------------------------------------------------|----------|------------|----------|
| <b>CH<sub>4</sub></b>                           | 24.98    | 19.11      | 22.61    |
| <b>CO<sub>2</sub></b>                           | 49.48    | 55.65      | 54.22    |
| <b>C<sub>2</sub></b>                            | 10.74    | 11.60      | 10.52    |
| <b>C<sub>3</sub></b>                            | 8.73     | 8.10       | 7.07     |
| <b>C<sub>4</sub></b>                            | 3.87     | 2.73       | 2.61     |
| <b>C<sub>5</sub></b>                            | 1.24     | 0.73       | 0.68     |
| <b>C<sub>6</sub><sup>+</sup></b>                | 0.41     | 1.29       | 1.60     |
| <b>H<sub>2</sub></b>                            | 0.55     | 0.81       | 0.68     |

**Figure 5.15:** Variation of gas product distribution of SCTE at 400°C (by weight percentage)

Variation of gas product distribution of SCTE of activated sludge at 425°C was given by volume in Table 5.18 and Figure 5.16. According to these results, when the solvent/solid ratio increased, the amount of CH<sub>4</sub> decreases, CO<sub>2</sub> and H<sub>2</sub> increases, C<sub>2</sub> decreases by volume.

Variation of gas product distribution of SCTE of activated sludge at 425°C was given by weight in Table 5.19 and Figure 5.17. When the solvent/solid ratio increased, the amount of CH<sub>4</sub> decreases, CO<sub>2</sub> increases, H<sub>2</sub> increases slightly and C<sub>2</sub> increases by weight.

Effect of solvent/solid ratio on gas product distribution was examined at two different temperatures to make results definite. If the results are generalized, there was a decreasing tendency in both volume and weight percentages of CH<sub>4</sub> and C<sub>2</sub> and increasing tendency of CO<sub>2</sub> and H<sub>2</sub> by increasing solvent/solid ratio.

Also, comparison of gas product distributions between two temperatures can be made by observing changes. For example, volume percentage of CO<sub>2</sub> decreases, CH<sub>4</sub> and H<sub>2</sub> increases at every solvent/solid ratio by increasing temperature (Table 5.18 and 5.19). As the temperature increases, the C<sub>2</sub>-C<sub>6</sub><sup>+</sup> products converted into smaller hydrocarbons and the amount of CH<sub>4</sub> increases.

**Table 5.18:** Variation of gas product distribution at 425°C for SCTE (by volume percentage)

| <b>Solvent/Solid Ratio</b><br><b>Components</b> | <b>1</b> | <b>1.5</b> | <b>3</b> |
|-------------------------------------------------|----------|------------|----------|
| <b>CH<sub>4</sub></b>                           | 55.02    | 40.73      | 33.65    |
| <b>CO<sub>2</sub></b>                           | 25.76    | 19.93      | 25.77    |
| <b>C<sub>2</sub></b>                            | 9.36     | 12.29      | 9.23     |
| <b>C<sub>3</sub></b>                            | 2.60     | 6.17       | 4.14     |
| <b>C<sub>4</sub></b>                            | 0.44     | 1.59       | 1.05     |
| <b>C<sub>5</sub></b>                            | 1.09     | 0.33       | 0.54     |
| <b>C<sub>6</sub><sup>+</sup></b>                | 0.05     | 0.31       | 0.00     |
| <b>H<sub>2</sub></b>                            | 5.69     | 18.66      | 25.62    |

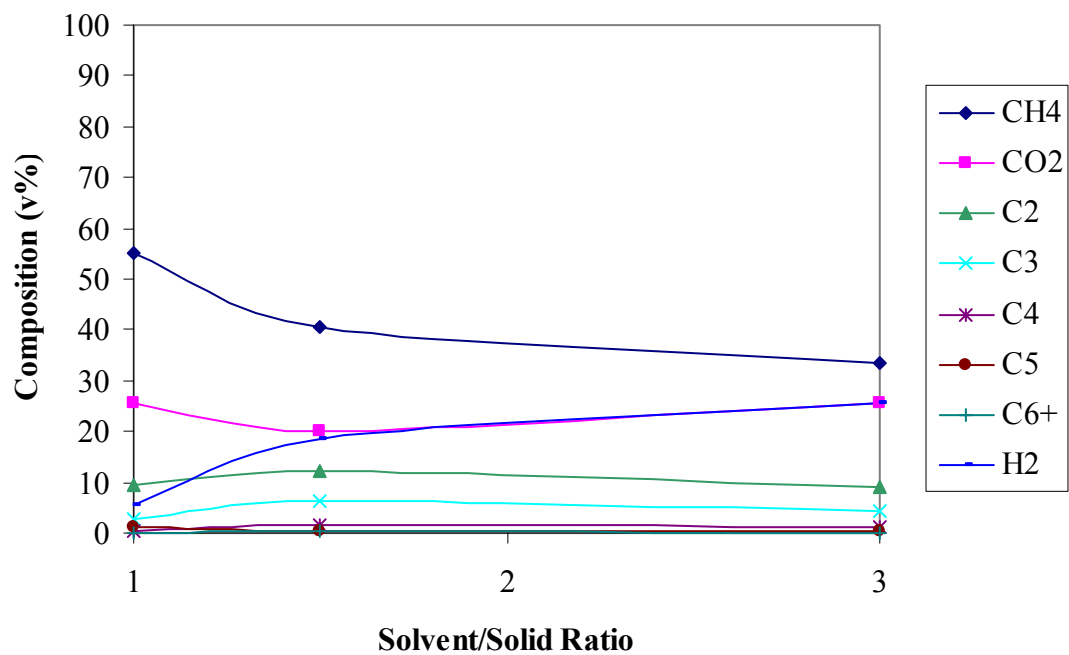


**Figure 5.16:** Variation of gas product distribution of SCTE at 425°C (by volume percentage)

**Table 5.19:** Variation of gas product distribution at 425°C for SCTE (by weight percentage)

| Solvent/Solid Ratio<br>Components | 1     | 1.5   | 3     |
|-----------------------------------|-------|-------|-------|
| CH <sub>4</sub>                   | 36.27 | 29.87 | 25.03 |
| CO <sub>2</sub>                   | 46.70 | 40.18 | 52.71 |
| C <sub>2</sub>                    | 9.25  | 13.51 | 10.30 |
| C <sub>3</sub>                    | 3.86  | 10.18 | 6.93  |
| C <sub>4</sub>                    | 0.86  | 3.49  | 2.34  |
| C <sub>5</sub>                    | 2.69  | 0.92  | 1.49  |
| C <sub>6</sub> <sup>+</sup>       | 0.14  | 1.02  | 0.00  |
| H <sub>2</sub>                    | 0.23  | 0.86  | 1.19  |

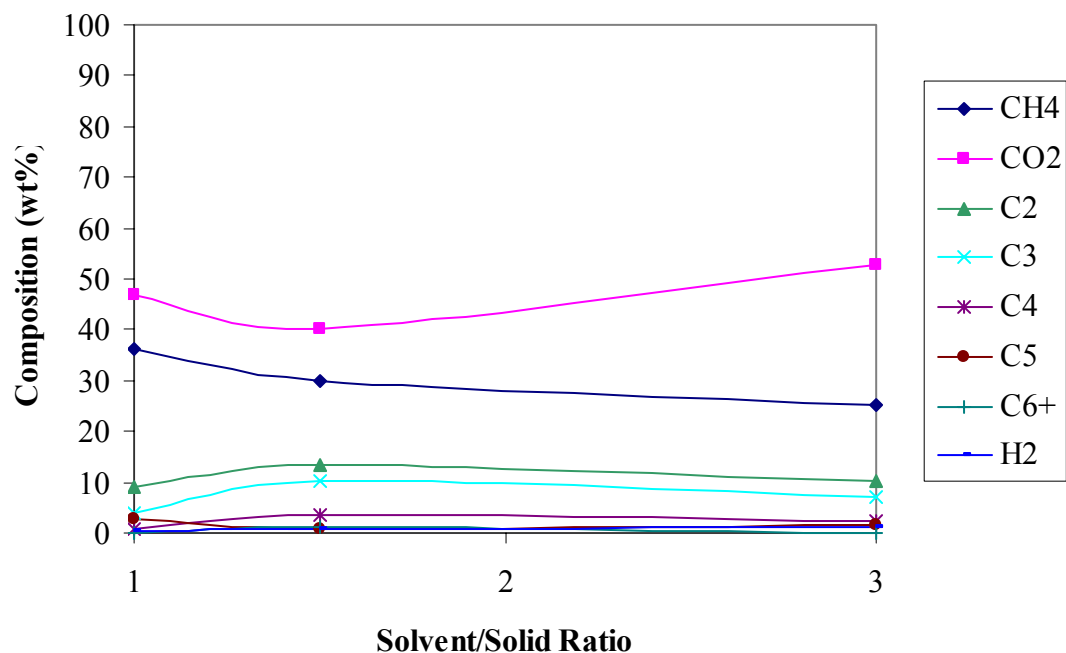


**Figure 5.17:** Variation of gas product distribution of SCTE at 425°C (by weight percentage)

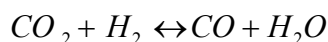
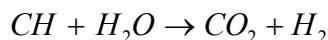
#### 5.2.4 Effect of temperature on gas product distribution

Effect of temperature on gas product distribution of SCWE and SCTE of activated sludge were examined when solvent/solid ratio was 1. Evaluations were made by volume percentage, volume, weight percentage and weight of gas products, respectively.

##### 5.2.4.1 Supercritical Water Extraction

Variation of SCWE gas product distribution with temperature was given by volume percentage when solvent/solid ratio was 1 (Table 5.20 and Figure 5.18). Major gas products were CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>. When the temperature increased from 350°C to 450°C, volume percentage of CH<sub>4</sub> in gas products increased from 9.81% to 18.07%, CO<sub>2</sub> decreased from 56.70% to 29.29% and H<sub>2</sub> increased from 15.69% to 26.44%.

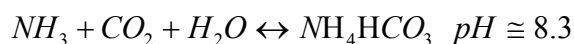
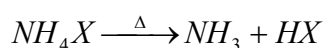
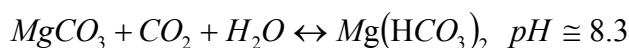
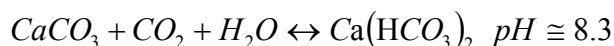
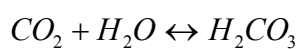
Possible reactions can be explained by;



In general;  $R - COOH \rightarrow CO_2 + RH$

For example;  $CH_3 - COOH \rightarrow CO_2 + CH_4$

Increase in the volume percentage of  $CH_4$  can be explained by conversion of high molecular weight hydrocarbons into low molecular hydrocarbons. This situation also confirmed by the increase in the  $C_2$ - $C_3$  products, which was formed by thermal cracking of heavier hydrocarbons. It was thought that, the volume of  $CO_2$  decreased; because of absorption of  $CO_2$  as calcium, magnesium and ammonium bicarbonates by increasing temperature. It was also proved by measuring pH of the extraction products. The pH of extraction products was 8. Possible absorption mechanisms of  $CO_2$ ;



Also, the increase in volume of  $H_2$  by increasing temperature can be explained by dehydrogenation of saturates or  $H_2$  can be separated from polycyclic structures by causing it to be aromatized.

There was an extreme situation, which was the critical condition. (For water,  $T_c$ :  $375^\circ C$  and  $P_c$ : 220 bar). There was a sudden decrease in the amount of  $CO_2$ .

In spite of reaction temperatures were low for gasification of activated sludge; volume percentage of CO was measured as 2.92% through 1.43% from  $350^\circ C$  to  $450^\circ C$ , respectively. As it is expected, there wasn't appreciable difference in amount of CO.

**Table 5.20:** Variation of gas product distribution with temperature for SCWE (Solvent/Solid Ratio: 1 and by volume percentage)

| Temperature (°C) \ Components | 350   | 375   | 400   | 425   | 450   |
|-------------------------------|-------|-------|-------|-------|-------|
| CH <sub>4</sub>               | 9.81  | 16.01 | 14.11 | 18.79 | 18.07 |
| CO <sub>2</sub>               | 56.70 | 34.57 | 40.69 | 36.83 | 29.29 |
| C <sub>2</sub>                | 4.86  | 9.64  | 6.46  | 7.94  | 9.13  |
| C <sub>3</sub>                | 5.60  | 8.17  | 6.36  | 3.72  | 8.16  |
| C <sub>4</sub>                | 3.26  | 5.06  | 3.76  | 2.81  | 4.84  |
| C <sub>5</sub>                | 0.94  | 2.27  | 1.22  | 1.20  | 1.87  |
| C <sub>6</sub> +              | 0.23  | 0.89  | 0.64  | 0.21  | 0.79  |
| H <sub>2</sub>                | 15.69 | 21.24 | 25.13 | 26.96 | 26.44 |
| CO                            | 2.92  | 2.16  | 1.62  | 1.55  | 1.43  |

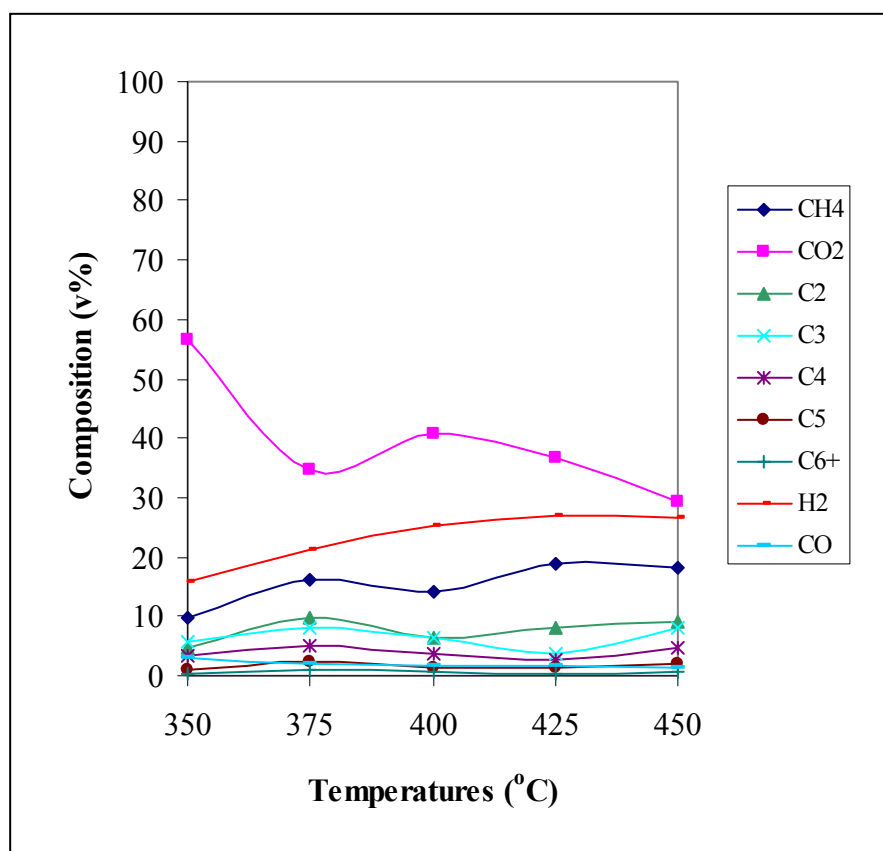


**Figure 5.18:** Variation of gas product distribution of SCWE with temperature (Solvent/Solid Ratio: 1 and by volume percentage)

Variation of SCWE gas product distribution with temperature was given by volume when solvent/solid ratio was 1. (Table 5.21 and Figure 5.19). When the temperature increased from 350°C to 450°C, volume of CH<sub>4</sub> in gas products increased from 108.91 mL. to 352.29 mL., CO<sub>2</sub> decreased from 629.33 mL. to 571.12 mL. and H<sub>2</sub> increased from 174.11 mL. to 515.64 mL. Volume of CO was measured as 32.41 mL. through 27.89 mL. from 350°C to 450°C, respectively. There wasn't appreciable difference in volume of CO.

**Table 5.21:** Variation of gas product distribution with temperature for SCWE (Solvent/Solid Ratio: 1 and by volume of gas, mL)

| <b>Temperature (°C)</b><br><b>Components</b> | <b>350</b> | <b>375</b> | <b>400</b> | <b>425</b> | <b>450</b> |
|----------------------------------------------|------------|------------|------------|------------|------------|
| <b>CH<sub>4</sub></b>                        | 108.91     | 252.92     | 231.48     | 317.59     | 352.29     |
| <b>CO<sub>2</sub></b>                        | 629.33     | 546.23     | 667.40     | 622.44     | 571.12     |
| <b>C<sub>2</sub></b>                         | 53.90      | 152.24     | 105.96     | 134.18     | 177.96     |
| <b>C<sub>3</sub></b>                         | 62.19      | 129.03     | 104.28     | 62.80      | 159.05     |
| <b>C<sub>4</sub></b>                         | 36.15      | 80.00      | 61.63      | 47.41      | 94.32      |
| <b>C<sub>5</sub></b>                         | 10.39      | 35.79      | 20.00      | 20.26      | 36.38      |
| <b>C<sub>6</sub><sup>+</sup></b>             | 2.60       | 14.05      | 10.51      | 3.54       | 15.39      |
| <b>H<sub>2</sub></b>                         | 174.11     | 335.61     | 412.16     | 455.59     | 515.64     |
| <b>CO</b>                                    | 32.41      | 34.13      | 26.57      | 26.20      | 27.89      |
| <b>Total (mL)</b>                            | 1110       | 1580       | 1640       | 1690       | 1950       |

Total volume of gas products were increased from 1110 mL. to 1950 mL. by increasing temperature from 350°C to 450°C. That is, conversion of liquid hydrocarbons into gas products (lighter ones) increases by increasing temperature.

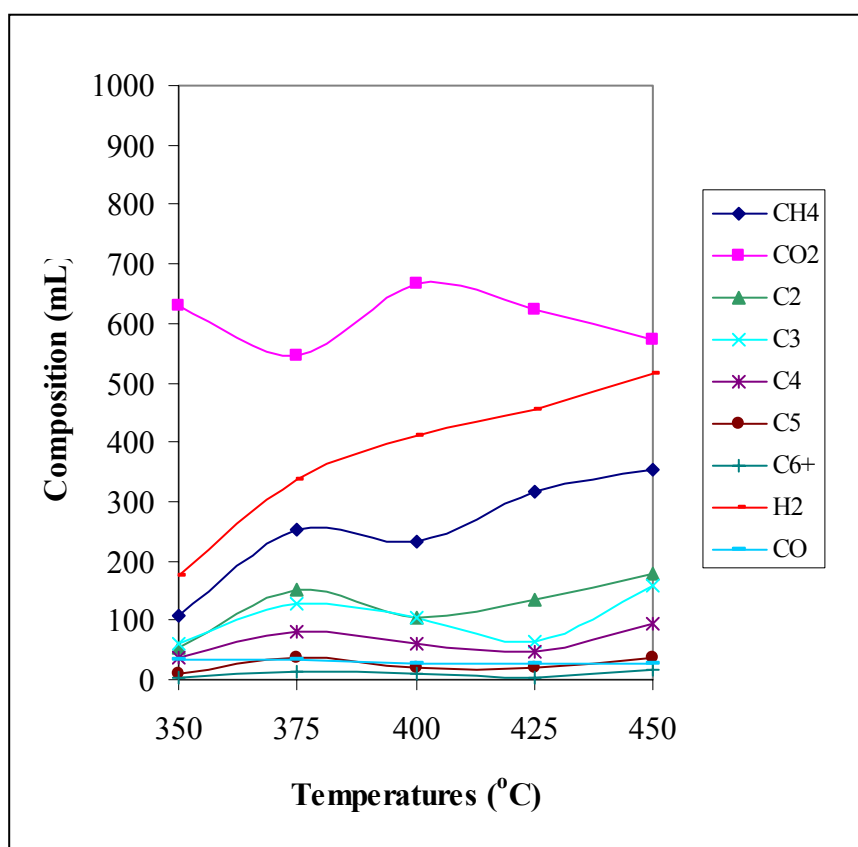


**Figure 5.19:** Variation of gas product distribution of SCWE with temperature (Solvent/Solid Ratio: 1 and by volume of gas, mL)

Variation of SCWE gas product distribution with temperature was given by weight percentage when solvent/solid ratio was 1. (Table 5.22 and Figure 5.20). When the temperature increased from 350°C to 450°C, weight percentage of CH<sub>4</sub> in gas products increased from 4.76% to 11.30%, CO<sub>2</sub> decreased from 75.67% to 50.38% and H<sub>2</sub> increased from 0.48% to 1.03%. Weight percentage of CO was calculated as 2.48% through 1.57% from 350°C to 450°C, respectively. There wasn't appreciable difference in weight percentage of CO.

**Table 5.22:** Variation of gas product distribution with temperature for SCWE (Solvent/Solid Ratio: 1 and by weight percentage)

| Temperature (°C) \ Components | 350   | 375   | 400   | 425   | 450   |
|-------------------------------|-------|-------|-------|-------|-------|
| CH <sub>4</sub>               | 4.76  | 9.06  | 8.15  | 11.85 | 11.30 |
| CO <sub>2</sub>               | 75.67 | 53.80 | 64.63 | 63.86 | 50.38 |
| C <sub>2</sub>                | 3.54  | 8.18  | 5.60  | 7.51  | 8.56  |
| C <sub>3</sub>                | 6.12  | 10.40 | 8.26  | 5.27  | 11.48 |
| C <sub>4</sub>                | 4.74  | 8.60  | 6.51  | 5.31  | 9.08  |
| C <sub>5</sub>                | 1.70  | 4.81  | 2.64  | 2.83  | 4.38  |
| C <sub>6</sub> +              | 0.51  | 2.26  | 1.67  | 0.59  | 2.22  |
| H <sub>2</sub>                | 0.48  | 0.75  | 0.91  | 1.06  | 1.03  |
| CO                            | 2.48  | 2.14  | 1.64  | 1.71  | 1.57  |

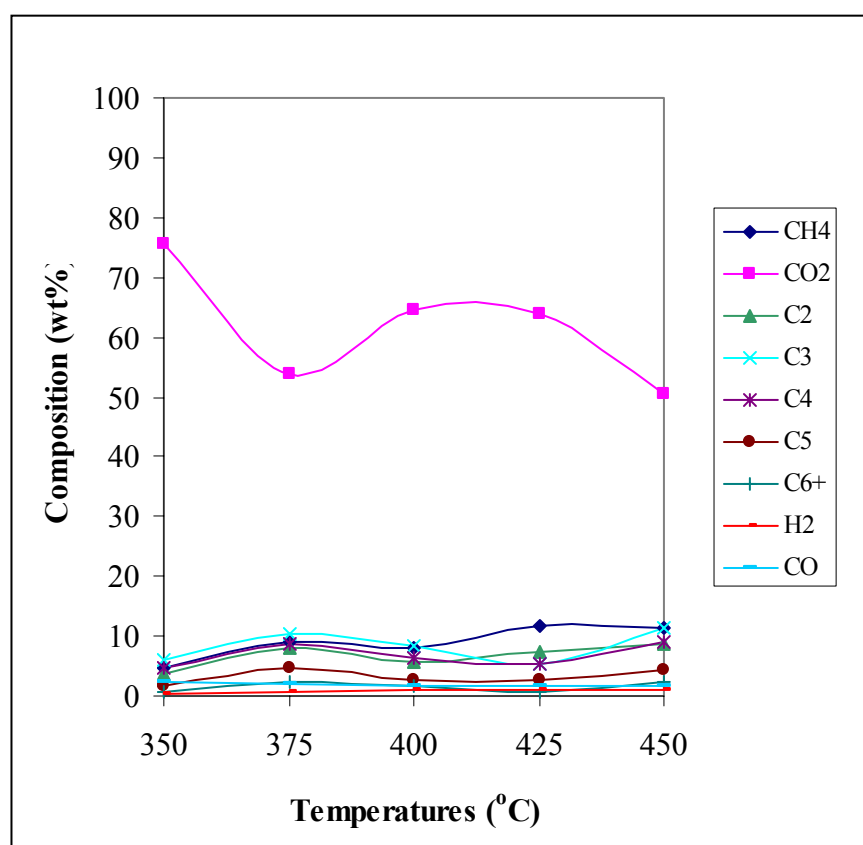


**Figure 5.20:** Variation of gas product distribution of SCWE with temperature (Solvent/Solid Ratio: 1 and by weight percentage)

Variation of SCWE gas product distribution with temperature was given by weight when solvent/solid ratio was 1. (Table 5.23 and Figure 5.21). When the temperature increased from 350°C to 450°C, weight of CH<sub>4</sub> in gas products increased from 0.07 g to 0.23, CO<sub>2</sub> decreased from 1.08 g to 1.03 g and H<sub>2</sub> increased from 0.01 g to 0.02 g. Weight of CO was calculated as 0.04 g through 0.03 from 350°C to 450°C, respectively. As it is expected, there wasn't appreciable difference in weight of CO.

**Table 5.23:** Variation of gas product distribution with temperature for SCWE (Solvent/Solid Ratio: 1 and by weight of gas, g)

| <b>Temperature (°C)</b><br><b>Components</b> | <b>350</b> | <b>375</b> | <b>400</b> | <b>425</b> | <b>450</b> |
|----------------------------------------------|------------|------------|------------|------------|------------|
| <b>CH<sub>4</sub></b>                        | 0.07       | 0.16       | 0.15       | 0.23       | 0.23       |
| <b>CO<sub>2</sub></b>                        | 1.08       | 0.98       | 1.21       | 1.22       | 1.03       |
| <b>C<sub>2</sub></b>                         | 0.05       | 0.15       | 0.10       | 0.14       | 0.17       |
| <b>C<sub>3</sub></b>                         | 0.09       | 0.19       | 0.15       | 0.10       | 0.23       |
| <b>C<sub>4</sub></b>                         | 0.07       | 0.16       | 0.12       | 0.10       | 0.19       |
| <b>C<sub>5</sub></b>                         | 0.02       | 0.09       | 0.05       | 0.05       | 0.09       |
| <b>C<sub>6</sub>+</b>                        | 0.01       | 0.04       | 0.03       | 0.01       | 0.05       |
| <b>H<sub>2</sub></b>                         | 0.01       | 0.01       | 0.02       | 0.02       | 0.02       |
| <b>CO</b>                                    | 0.04       | 0.04       | 0.03       | 0.03       | 0.03       |
| <b>Total (g)</b>                             | 1.43       | 1.82       | 1.87       | 1.91       | 2.04       |

Total weight of gas products were increased from 1.43 g to 2.04 g by increasing temperature from 350°C to 450°C. That is, conversion of liquid hydrocarbons into gas products (lighter ones) increases by increasing temperature.

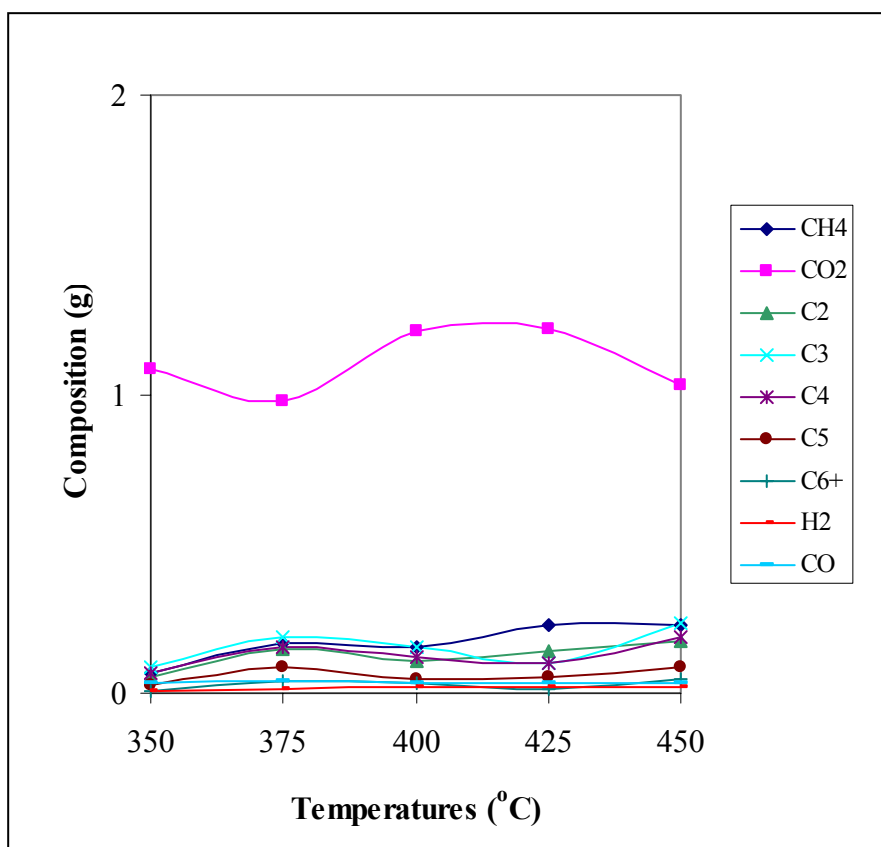


**Figure 5.21:** Variation of gas product distribution of SCWE with temperature (Solvent/Solid Ratio: 1 and by weight of gas, g)

#### 5.2.4.2 Supercritical Toluene Extraction

Variation of SCTE gas product distribution with temperature was given by volume percentage when solvent/solid ratio was 1. (Table 5.24 and Figure 5.22). Major gas products were CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub> and C<sub>2</sub>. When the temperature increased from 300°C to 450°C, volume percentage of CH<sub>4</sub> in gas products increased from 28.55% to 55.13% and CO<sub>2</sub> decreased from 37.55% to 22.65%.

**Table 5.24:** Variation of gas product distribution with temperature for SCTE (Solvent/Solid Ratio: 1 and by volume percentage)

| Temperature (°C) \ Components | 300   | 350   | 375   | 400   | 425   | 450   |
|-------------------------------|-------|-------|-------|-------|-------|-------|
| CH <sub>4</sub>               | 28.55 | 26.80 | 33.73 | 38.74 | 55.02 | 55.13 |
| CO <sub>2</sub>               | 37.55 | 38.00 | 30.24 | 27.90 | 25.76 | 22.65 |
| C <sub>2</sub>                | 12.09 | 11.48 | 12.07 | 11.10 | 9.36  | 10.51 |
| C <sub>3</sub>                | 6.26  | 6.46  | 6.29  | 6.01  | 2.60  | 1.93  |
| C <sub>4</sub>                | 2.23  | 2.05  | 1.76  | 2.00  | 0.44  | 0.40  |
| C <sub>5</sub>                | 0.75  | 0.26  | 0.32  | 0.51  | 1.09  | 0.16  |
| C <sub>6</sub> +              | 0.55  | 0.21  | 0.03  | 0.14  | 0.05  | 0.11  |
| H <sub>2</sub>                | 12.03 | 14.73 | 15.56 | 13.60 | 5.69  | 9.11  |

When the temperature increased from 300°C to 375°C, volume percentage of H<sub>2</sub> increased from 12.03% to 15.56% and then suddenly decreased in H<sub>2</sub> from 15.56% to 9.11%. This decrease can be explained by the formation of CH<sub>4</sub> in this temperature interval. That is, formed H<sub>2</sub> was spent for saturation of unsaturated hydrocarbons.

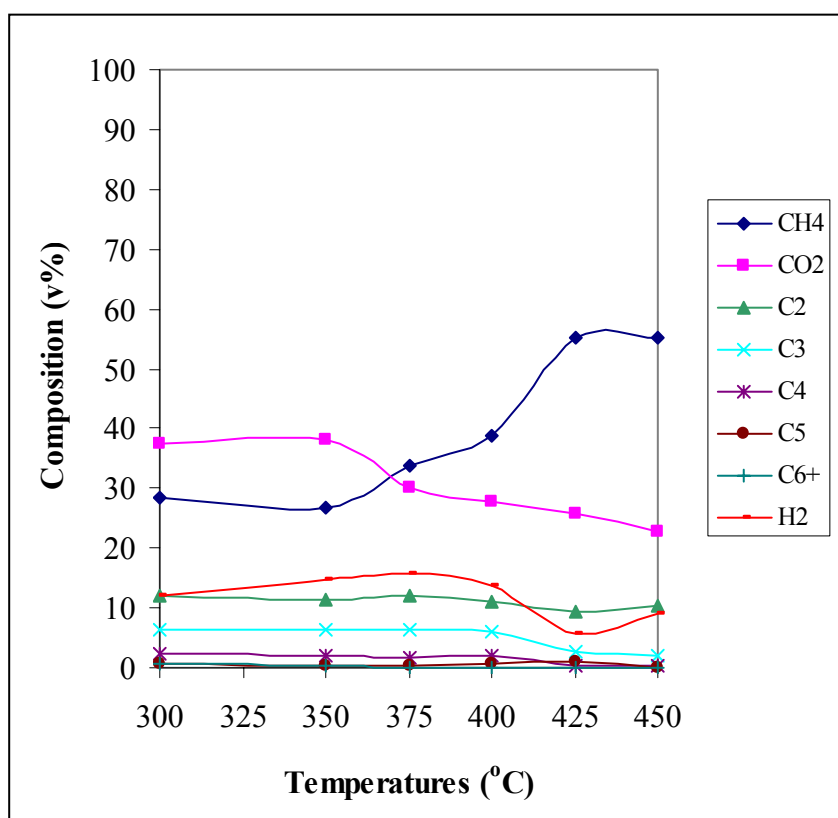


**Figure 5.22:** Variation of gas product distribution of SCTE with temperature (Solvent/Solid Ratio: 1 and by volume percentage)

Variation of SCTE gas product distribution with temperature was given by volume of gas when solvent/solid ratio was 1. (Table 5.25 and Figure 5.23). When the temperature increased from 300°C to 450°C, volume of CH<sub>4</sub> in gas products increased from 179.8 mL. to 1797.2 mL., CO<sub>2</sub> increased from 236.5 mL. to 738.5 mL. and H<sub>2</sub> increased from 75.8 mL. to 296.8 mL.

**Table 5.25:** Variation of gas product distribution with temperature for SCTE (Solvent/Solid Ratio: 1 and by volume of gas, mL)

| Temperature (°C)<br>Components | 300   | 350   | 375   | 400   | 425    | 450    |
|--------------------------------|-------|-------|-------|-------|--------|--------|
| CH <sub>4</sub>                | 179.8 | 328.4 | 487.3 | 761.2 | 1414.0 | 1797.2 |
| CO <sub>2</sub>                | 236.5 | 465.5 | 437.0 | 548.3 | 662.0  | 738.5  |
| C <sub>2</sub>                 | 76.2  | 140.7 | 174.4 | 218.1 | 240.4  | 342.6  |
| C <sub>3</sub>                 | 39.5  | 79.2  | 91.0  | 118.2 | 66.8   | 62.8   |
| C <sub>4</sub>                 | 14.1  | 25.1  | 25.4  | 39.3  | 11.2   | 13.0   |
| C <sub>5</sub>                 | 4.7   | 3.2   | 4.6   | 10.1  | 28.0   | 5.4    |
| C <sub>6</sub> <sup>+</sup>    | 3.4   | 2.6   | 0.4   | 2.8   | 1.3    | 3.7    |
| H <sub>2</sub>                 | 75.8  | 180.4 | 224.8 | 267.1 | 146.3  | 296.8  |
| Total (mL)                     | 630   | 1225  | 1445  | 1965  | 2570   | 3260   |

Total volume of gas products were increased from 630 mL. to 3260 mL. by increasing temperature from 300°C to 450°C. That is, liquid hydrocarbons were converted into gas products (lighter ones) by increasing temperature. Also, yield of gas products in SCTE were higher than the SCWE of activated sludge at every temperature. (Table 5.21 and 5.27)

Variation of SCTE gas product distribution with temperature was given by weight percentage when solvent/solid ratio was 1. (Table 5.26 and Figure 5.24). When the temperature increased from 300°C to 450°C, weight percentage of CH<sub>4</sub> in gas products increased from 17.85% to 43.76% and CO<sub>2</sub> decreased from 64.56% to 49.44%.

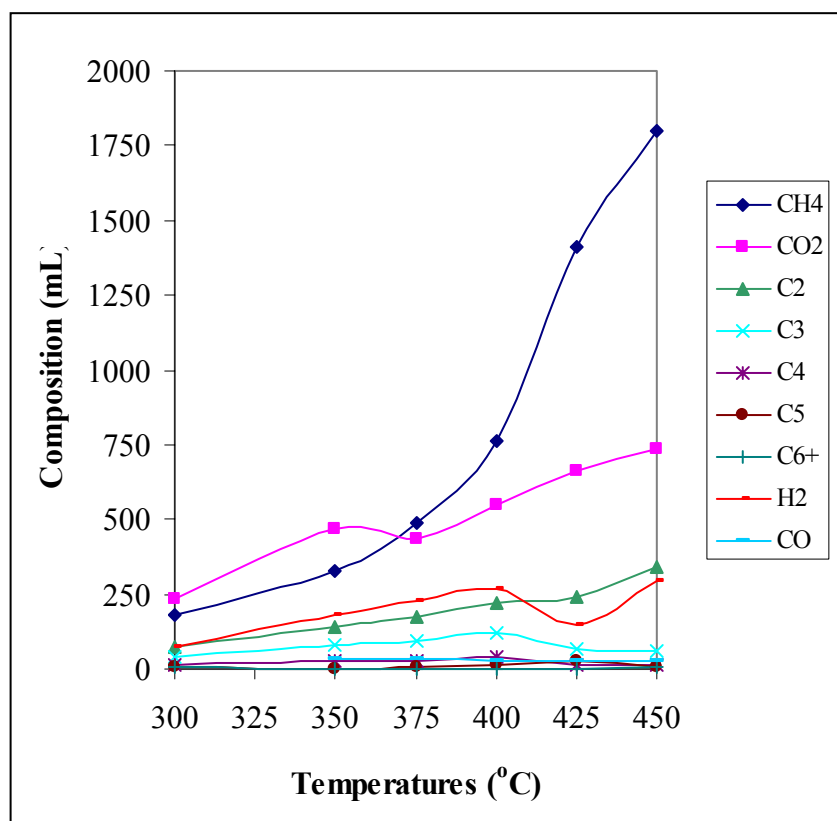


**Figure 5.23:** Variation of gas product distribution of SCTE with temperature (Solvent/Solid Ratio: 1 and by volume of gas, mL)

**Table 5.26:** Variation of gas product distribution with temperature for SCTE (Solvent/Solid Ratio: 1 and by weight percentage)

| Temperature (°C)<br>Components | 300   | 350   | 375   | 400   | 425   | 450   |
|--------------------------------|-------|-------|-------|-------|-------|-------|
| CH <sub>4</sub>                | 17.85 | 17.16 | 24.10 | 27.72 | 39.58 | 43.76 |
| CO <sub>2</sub>                | 64.56 | 66.92 | 59.42 | 54.91 | 50.96 | 49.44 |
| C <sub>2</sub>                 | 0.83  | 0.85  | 0.95  | 0.96  | 0.96  | 1.06  |
| C <sub>3</sub>                 | 8.81  | 9.31  | 10.12 | 9.68  | 4.21  | 3.44  |
| C <sub>4</sub>                 | 4.19  | 3.93  | 3.77  | 4.29  | 0.94  | 0.95  |
| C <sub>5</sub>                 | 1.75  | 0.63  | 0.85  | 1.38  | 2.94  | 0.49  |
| C <sub>6</sub> +               | 1.53  | 0.60  | 0.08  | 0.45  | 0.16  | 0.41  |
| H <sub>2</sub>                 | 0.47  | 0.59  | 0.69  | 0.61  | 0.26  | 0.45  |

When the temperature increased from 300°C to 375°C, volume percentage of H<sub>2</sub> increased from 0.47% to 0.69% and then suddenly decreased in H<sub>2</sub> from 0.69% to 0.45%. This decrease can be explained by the formation of CH<sub>4</sub> in this temperature interval. That is, formed H<sub>2</sub> was spent for saturation of unsaturated hydrocarbons.

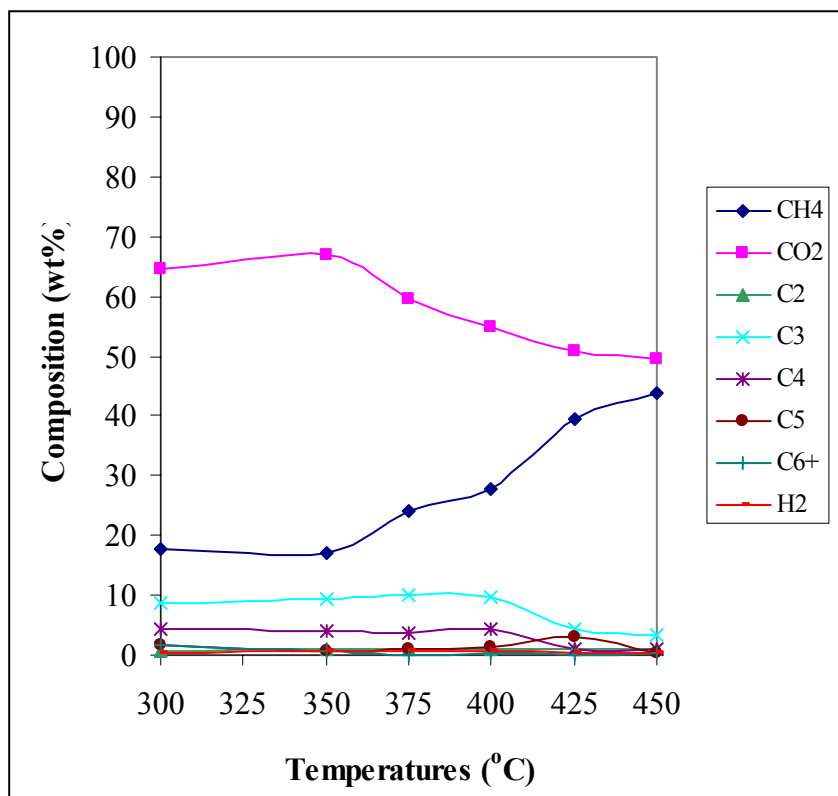


**Figure 5.24:** Variation of gas product distribution of SCTE with temperature (Solvent/Solid Ratio: 1 and by weight percentage)

Variation of SCTE gas product distribution with temperature was given by weight when solvent/solid ratio was 1. (Table 5.27 and Figure 5.25). When the temperature increased from 300°C to 450°C, weight of CH<sub>4</sub> in gas products increased from 0.16 g to 1.32 g, CO<sub>2</sub> increased from 0.57 g to 1.49 g and H<sub>2</sub> increased from 0.00 g to 0.01 g.

**Table 5.27:** Variation of gas product distribution with temperature for SCTE (Solvent/Solid Ratio: 1 and by weight of gas, g)

| Temperature (°C) \ Components | 300         | 350         | 375         | 400         | 425         | 450         |
|-------------------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| CH <sub>4</sub>               | 0.16        | 0.24        | 0.37        | 0.54        | 1.11        | 1.32        |
| CO <sub>2</sub>               | 0.57        | 0.93        | 0.92        | 1.07        | 1.43        | 1.49        |
| C <sub>2</sub>                | 0.01        | 0.01        | 0.01        | 0.02        | 0.03        | 0.03        |
| C <sub>3</sub>                | 0.08        | 0.13        | 0.16        | 0.19        | 0.12        | 0.10        |
| C <sub>4</sub>                | 0.04        | 0.05        | 0.06        | 0.08        | 0.03        | 0.03        |
| C <sub>5</sub>                | 0.02        | 0.01        | 0.01        | 0.03        | 0.08        | 0.01        |
| C <sub>6</sub> +              | 0.01        | 0.01        | 0.00        | 0.01        | 0.00        | 0.01        |
| H <sub>2</sub>                | 0.00        | 0.01        | 0.01        | 0.01        | 0.01        | 0.01        |
| <b>Total (g)</b>              | <b>0.89</b> | <b>1.39</b> | <b>1.54</b> | <b>1.95</b> | <b>2.80</b> | <b>3.02</b> |

Total weight of gas products were increased from 0.89 g to 3.02 g by increasing temperature from 300°C to 450°C. Because, when temperature increases, liquid hydrocarbons are converted to gas products (lighter ones). At higher temperatures, amount of gas in SCTE were higher than SCWE of activated sludge. (Table 5.23 and 5.27)

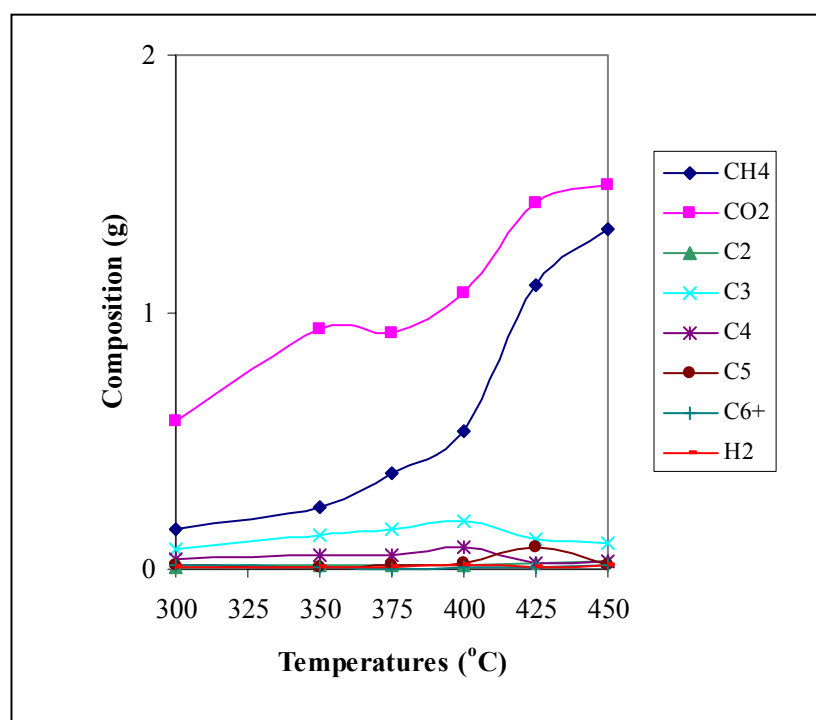


**Figure 5.25:** Variation of gas product distribution of SCTE with temperature (Solvent/Solid Ratio: 1 and by weight of gas, g)

### 5.2.5 Effect of temperature on liquid product distribution

After determination of composition and distribution of gas products of SCWE and SCTE of activated sludge, liquid products (extract) must be identified. Amount of oil, asphaltenes and preasphaltenes in extract were determined by weight percentages. Then, deasphalted oil was analyzed by IR spectrophotometer and change in aliphatic/aromatic ratios with temperature was calculated. After that, deasphalted oil was separated into aliphatic, aromatic and polar fractions by liquid absorption chromatography and aliphatic fractions were injected into gas chromatography to form simulated distillation curves. By this way, aliphatic fraction was separated into petroleum hydrocarbons according to their boiling points.

#### 5.2.5.1 Supercritical Water Extraction

Aliphatic fraction of SCWE oil was separated into gasoline, middle distillates and wide cut gas-oil by using gas chromatograms where the area of the peaks were summed at certain boiling point ranges (that is carbon numbers). When temperature increased from 350°C to 425°C, gasoline fraction decreased from 54.96 wt.% to 8.51 wt.%. In addition to this, amount of gasoline in extraction products decreased because of increasing extract yield with increasing temperature. Amount of gasoline fraction in activated sludge was 41 wt.%, 39 wt.%, 38.9 wt.% and 33 wt.% at 350°C, 375°C, 400°C and 425°C, respectively. As the gasoline fraction decreased, middle distillates and wide cut gas-oil fractions increased by temperature. (Table 5.28 and Figure 5.26)

**Table 5.28:** Aliphatic fraction of oil for SCWE

| <b>Temperature<br/>(°C)</b><br><b>Fraction (wt. %)</b> | <b>350</b> | <b>375</b> | <b>400</b> | <b>425</b> |
|--------------------------------------------------------|------------|------------|------------|------------|
| Gasoline                                               | 54.96      | 51.81      | 78.69      | 8.51       |
| Middle Distillate                                      | 44.88      | 47.97      | 21.04      | 90.03      |
| Wide cut gas-oil                                       | 0.16       | 0.22       | 0.27       | 1.46       |

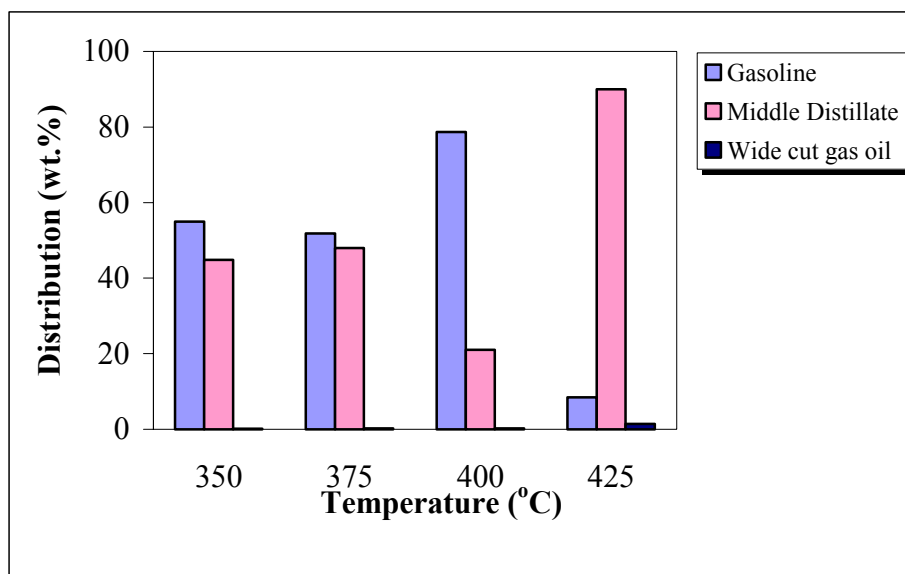


**Figure 5.26:** Variation of aliphatic fraction of SCWE oil

Simulated distillation curves of aliphatic fractions of oils obtained from SCWE of activated sludge were given in Figure 5.27. According to these curves, it is possible to identify products that were aliphatic fractions of oils and extracted at different temperatures. Mentioned petroleum hydrocarbons were fractionated by the help of these curves.

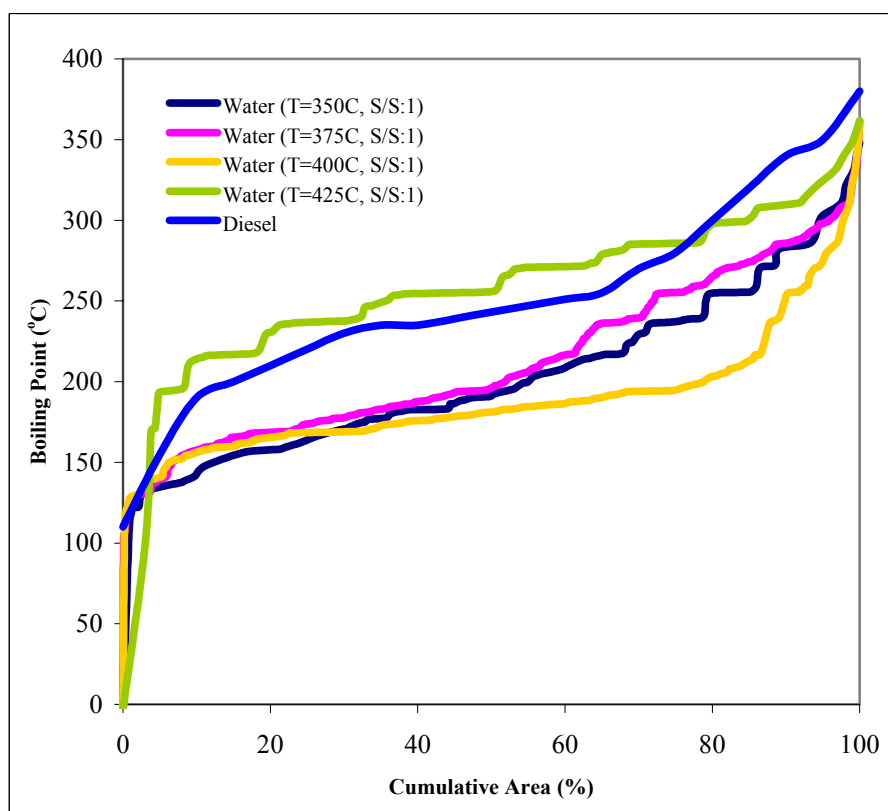


**Figure 5.27:** Simulated distillation curves of aliphatic fractions of oils obtained from SCWE of activated sludge

Change in aliphatic/aromatic ratios of deasphalted oil with temperature was calculated and given in Table 5.29. Aliphatic/aromatic ratio was increased by increasing temperature. It can be understood that, reactivity of water increased as the temperature increases and the effect of water into the structure of activated sludge increased. So, it prevents the formation of aromatic fractions and leads to the formation of aliphatic fractions.

**Table 5.29:** Aliphatic/Aromatic ratio of oil for SCWE

| Temperature (°C) | Aliphatic/Aromatic |
|------------------|--------------------|
| 350              | 2.51               |
| 375              | 2.67               |
| 400              | 2.65               |
| 425              | 4.05               |

IR spectras of deasphalted oils obtained by extraction of activated sludge at different temperatures were given in Figure 5.28, 5.29, 5.30 and 5.31. At specified wavenumber ranges the area of the peaks were calculated to obtain aliphatic/aromatic ratios.

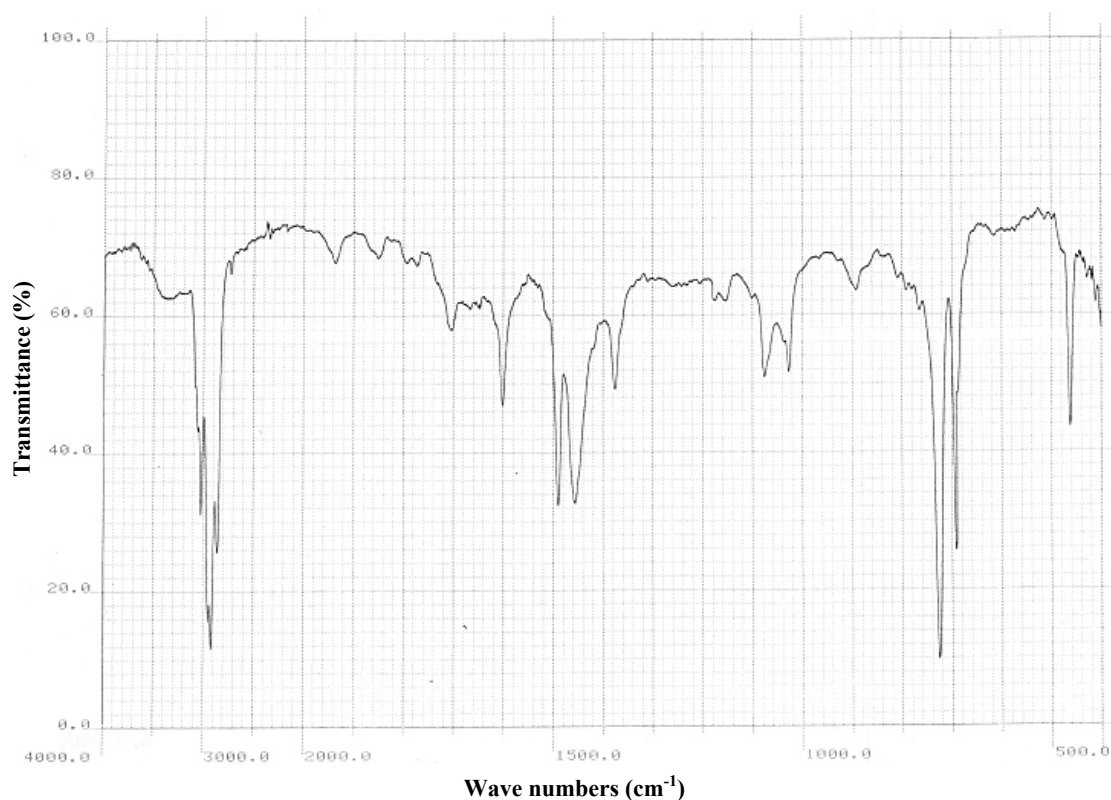


**Figure 5.28:** IR spectrum of deasphalted oil extracted with water at 350°C

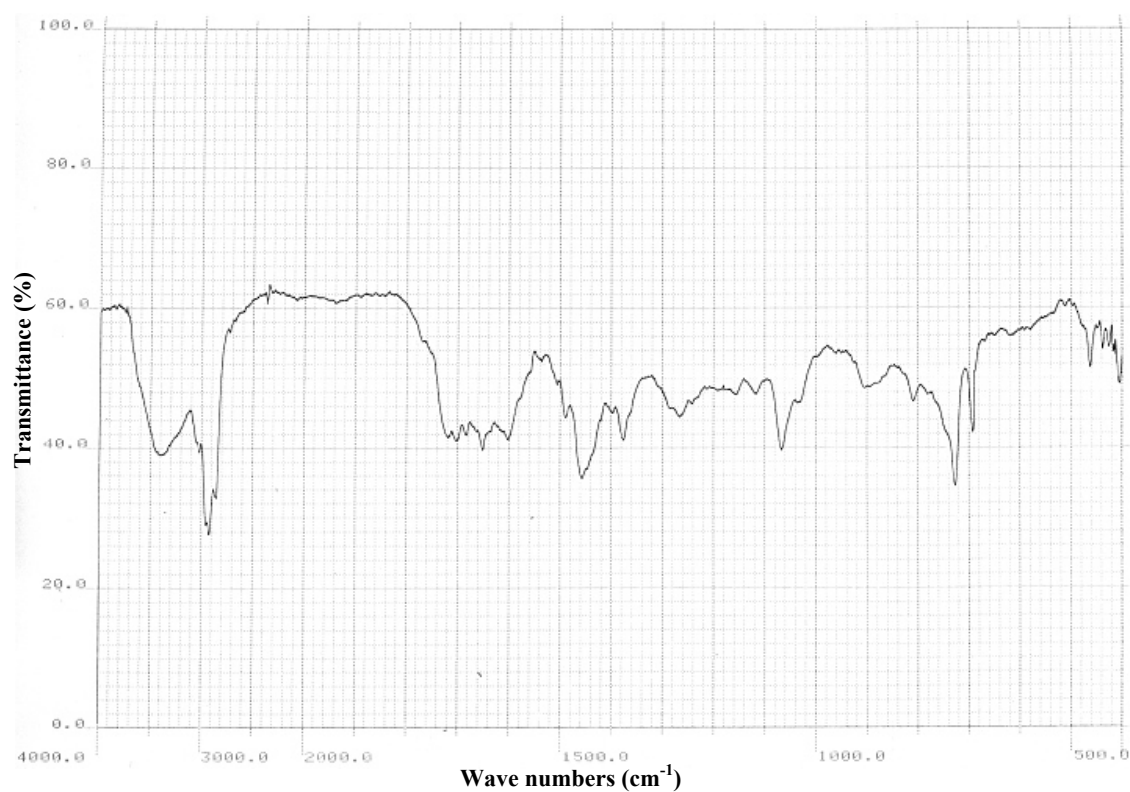


**Figure 5.29:** IR spectrum of deasphalted oil extracted with water at 375°C

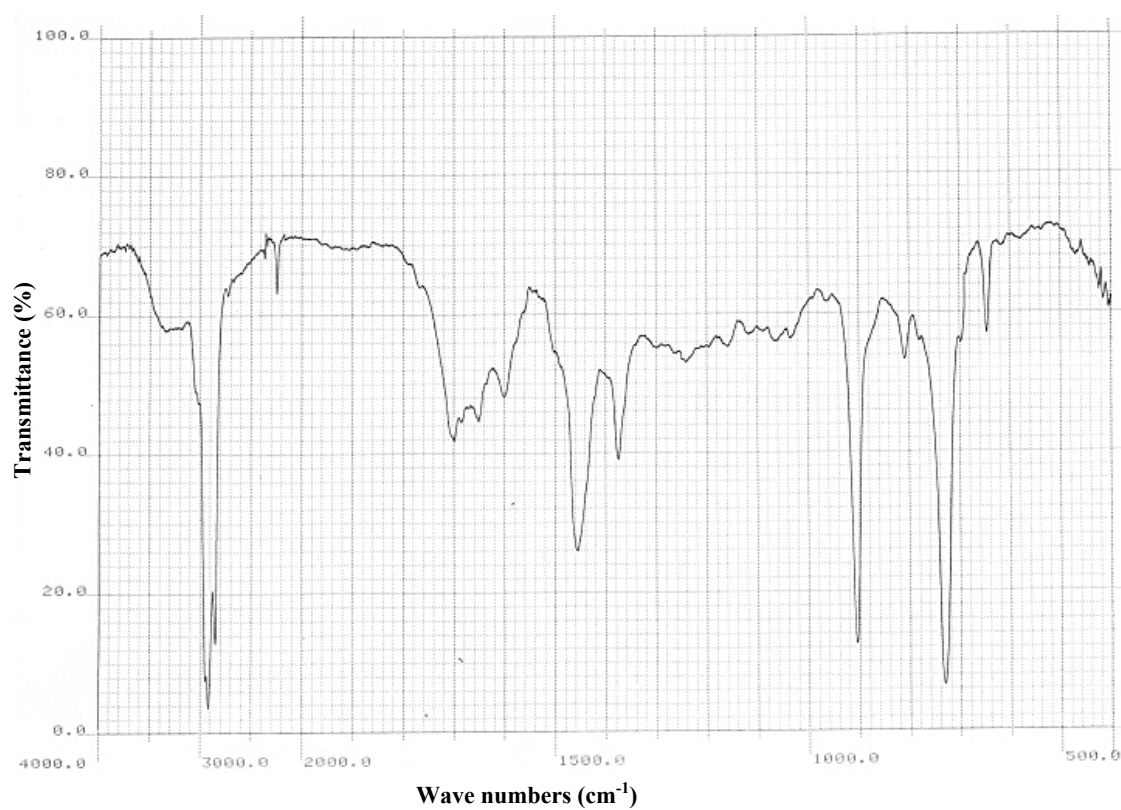


**Figure 5.30:** IR spectrum of deasphalted oil extracted with water at 400°C

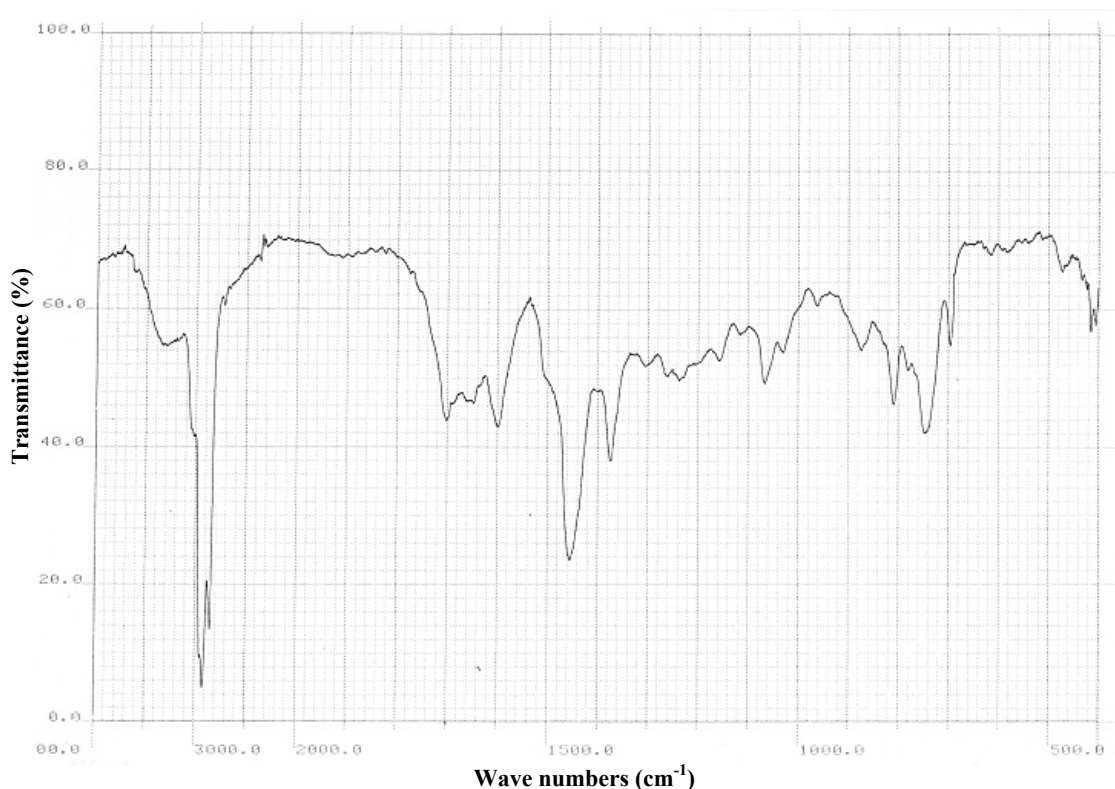


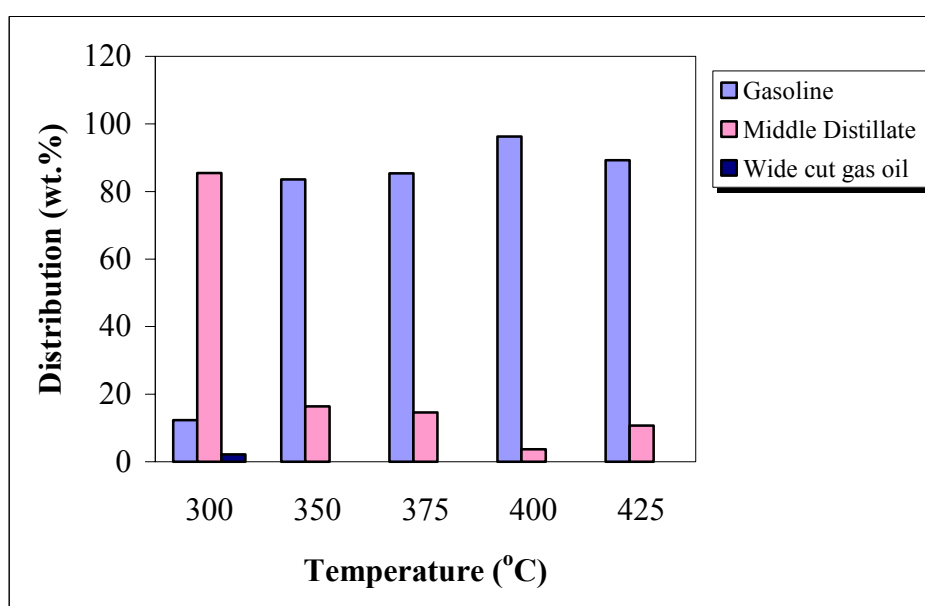
**Figure 5.31:** IR spectrum of deasphalted oil extracted with water at 425°

#### 5.2.5.2 Supercritical Toluene Extraction

Aliphatic fraction of SCTE oil was separated into gasoline, middle distillates and wide cut gas-oil by using gas chromatograms in same manner with SCWE. When temperature increased from 300°C to 425°C, gasoline fraction increased from 12.29 wt.% to 89.24 wt.%. In addition to this, amount of gasoline in extraction products decreased because of decreasing extract yield with increasing temperature. Amount of gasoline fraction in activated sludge was 5.53 wt.%, 35.02 wt.%, 32.37 wt.%, 35.15 wt.% and 27.07 wt.% at 300°C, 350°C, 375°C, 400°C and 425°C, respectively. As the gasoline fraction increased, middle distillates and wide cut gas-oil fractions decreased by temperature. (Table 5.30 and Figure 5.28)

**Table 5.30:** Aliphatic fraction of oil for SCTE

| <b>Temperature<br/>(°C)</b><br><b>Fraction<br/>(wt. %)</b> | <b>300</b> | <b>350</b> | <b>375</b> | <b>400</b> | <b>425</b> |
|------------------------------------------------------------|------------|------------|------------|------------|------------|
| Gasoline                                                   | 12.29      | 83.55      | 85.42      | 96.29      | 89.24      |
| Middle Distillate                                          | 85.49      | 16.45      | 14.58      | 3.71       | 10.76      |
| Wide cut gas-oil                                           | 2.22       | 0          | 0          | 0          | 0          |

**Figure 5.32:** Variation of aliphatic fraction of SCTE oil

Simulated distillation curves of aliphatic fractions of oils obtained from SCTE of activated sludge were given in Figure 5.29. According to these curves, it is possible to identify products that were aliphatic fractions of oils and extracted at different temperatures. Mentioned petroleum hydrocarbons were fractionated by the help of these curves.

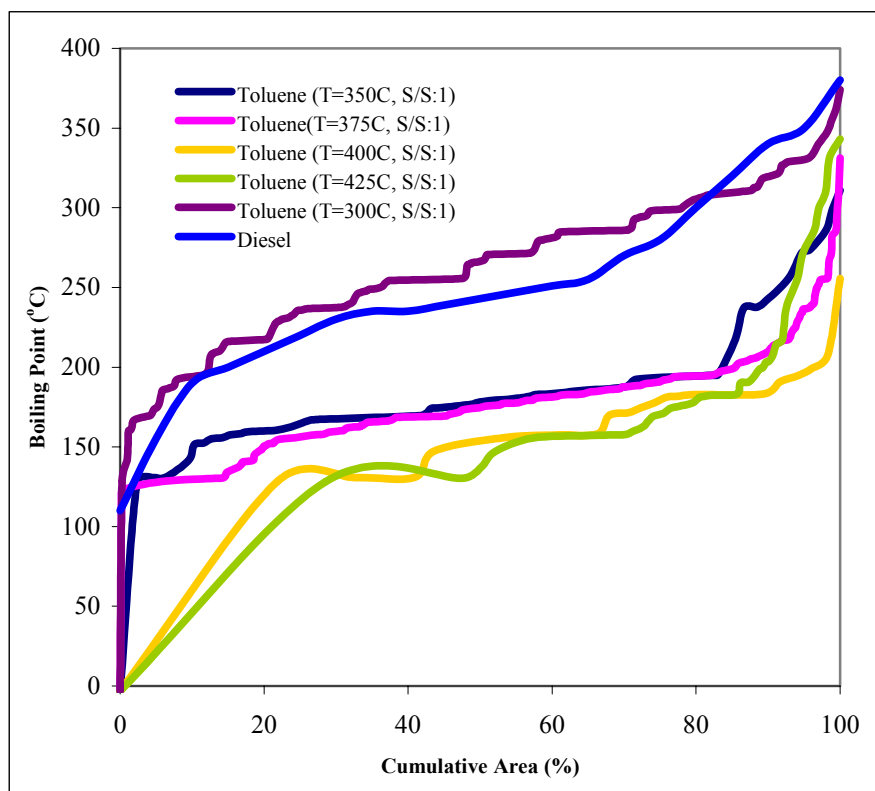


**Figure 5.33:** Simulated distillation curves of aliphatic fractions of oils obtained from SCTE of activated sludge

Change in aliphatic/aromatic ratios of deasphalted oil with temperature was calculated and given in Table 5.31. Aliphatic/aromatic ratio decreased by increasing temperature. Unlike water, toluene was not reactive, so the formation of aromatic fractions observed by increasing temperature.

**Table 5.31:** Aliphatic/Aromatic ratio of SCTE oil

| Temperature (°C) | Aliphatic/Aromatic |
|------------------|--------------------|
| <b>300</b>       | 3.58               |
| <b>350</b>       | 2.08               |
| <b>375</b>       | 1.98               |
| <b>400</b>       | 1.99               |
| <b>425</b>       | 1.65               |

IR spectras of deasphalted oils obtained by extraction of activated sludge at different temperatures were given in Figure 5.34 through 5.38. At specified wavenumber ranges the area of the peaks were calculated to obtain aliphatic/aromatic ratios.

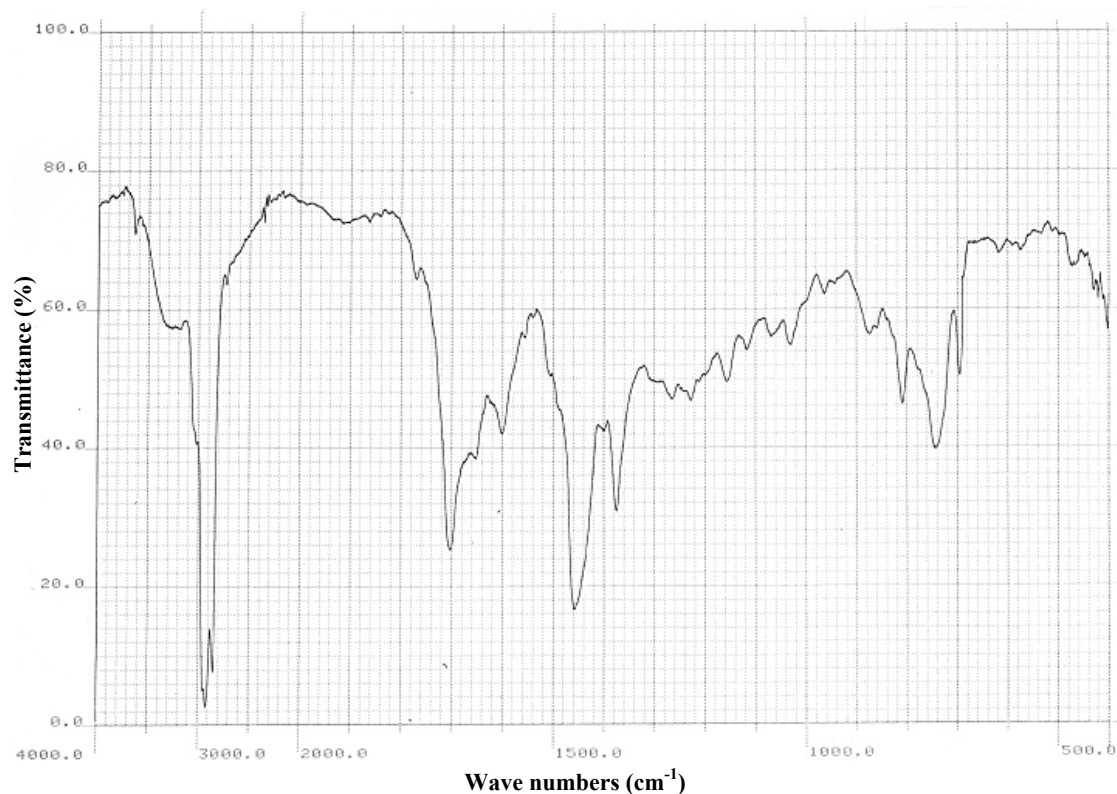


**Figure 5.34:** IR spectrum of deasphalted oil extracted with toluene at 300°C

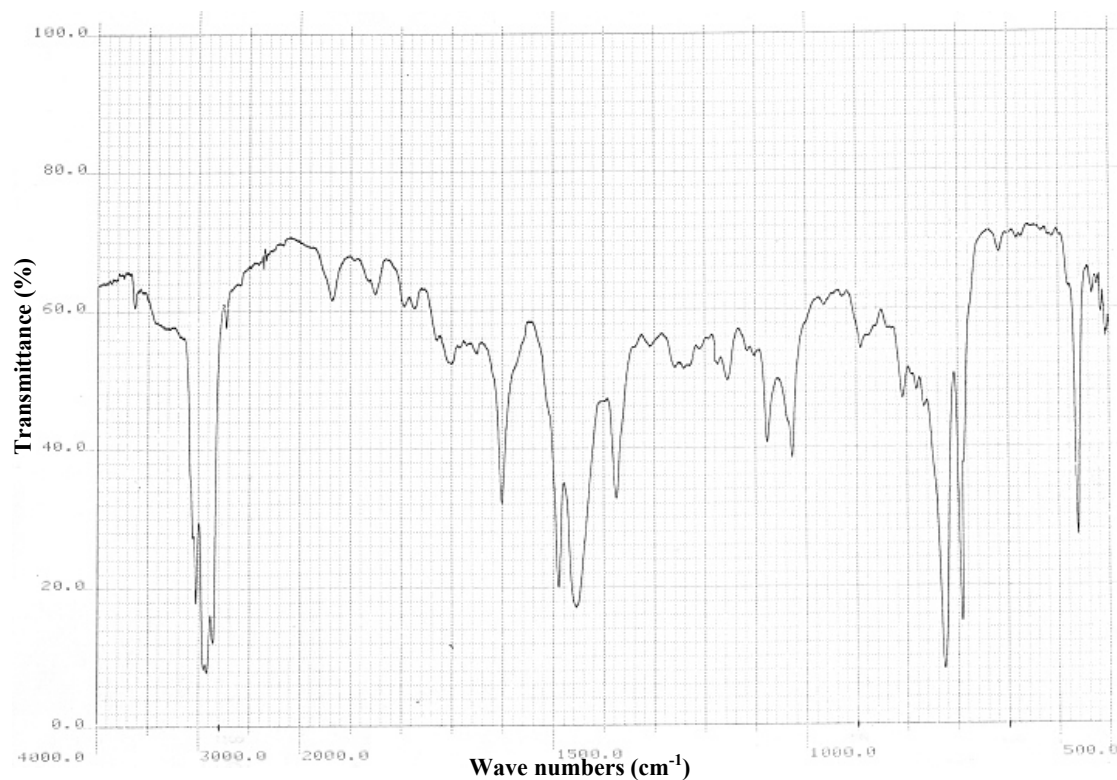


**Figure 5.35:** IR spectrum of deasphalted oil extracted with toluene at 350°C

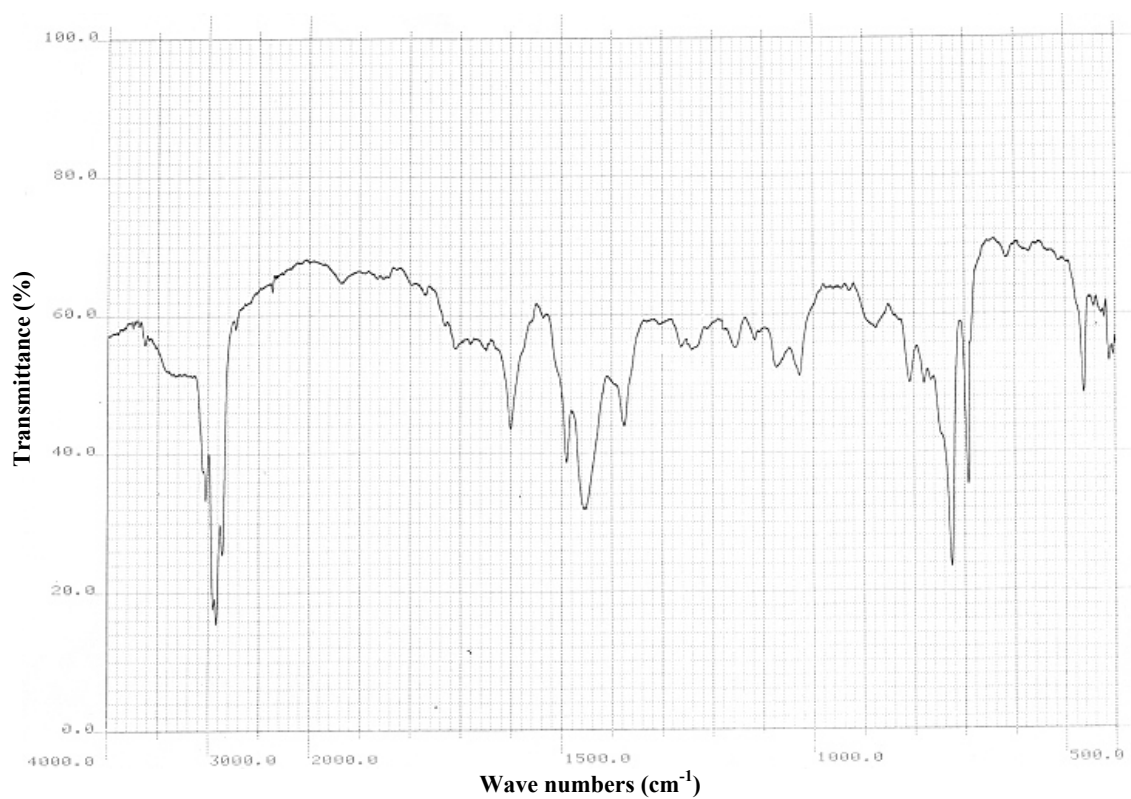


**Figure 5.36:** IR spectrum of deasphalted oil extracted with toluene at 375°C

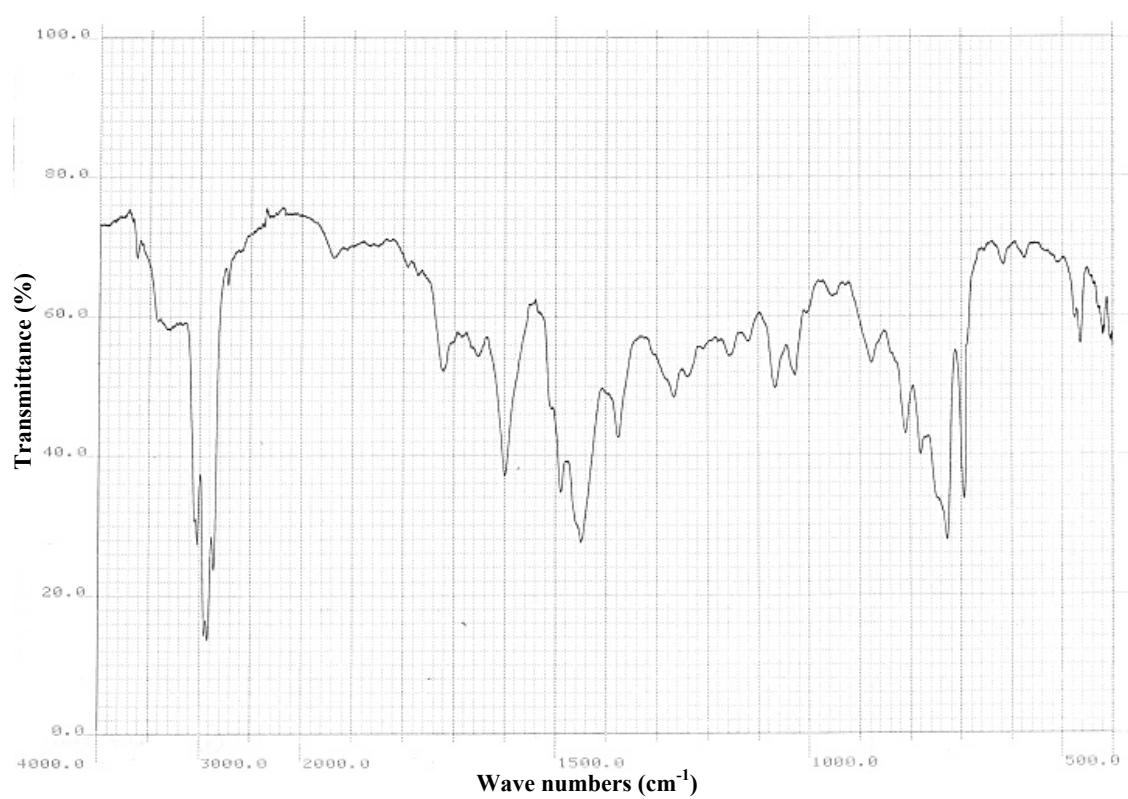


**Figure 5.37:** IR spectrum of deasphalted oil extracted with toluene at 400°C

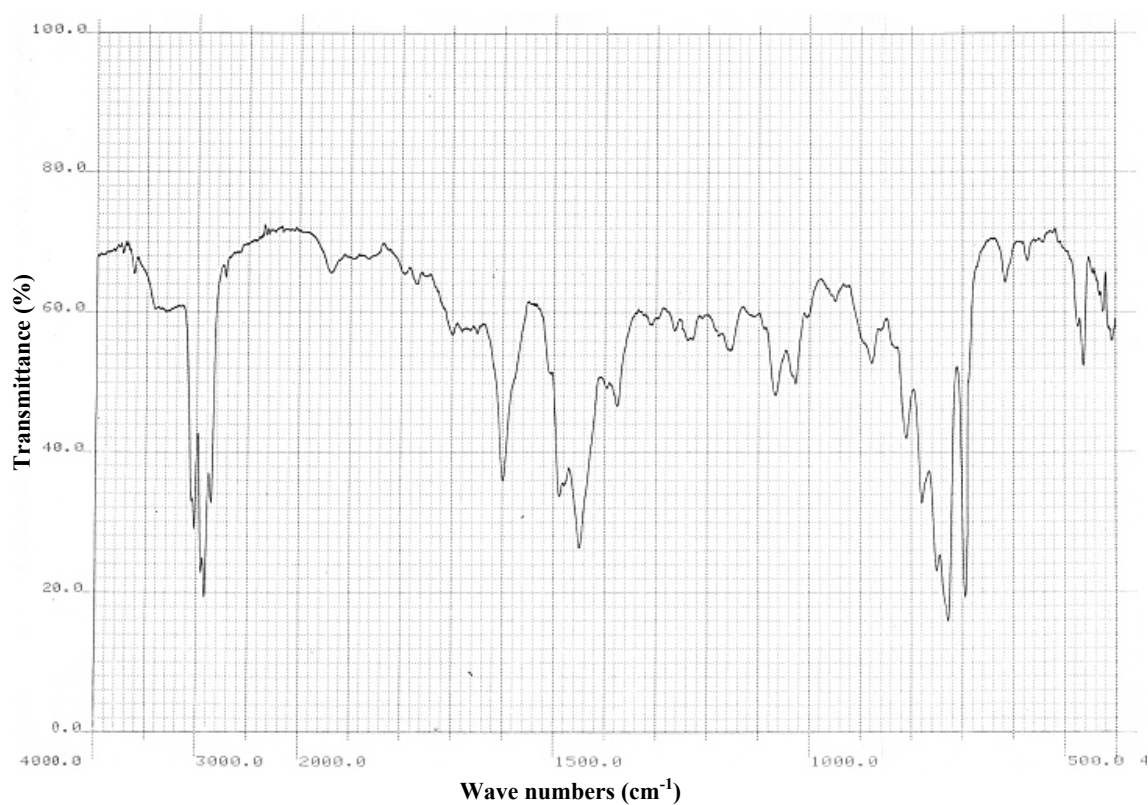


**Figure 5.38:** IR spectrum of deasphalted oil extracted with toluene at 425°C

## 6. CONCLUSION

SCFE is an innovative and effective destruction method for organic-rich wastewaters and sludges. A major advantage of SCFE systems are that they are capable of completely destroying organic compounds in a totally enclosed facility without producing harmful emissions. SCWE utilizes water above its critical point of 374°C and 22 MPa, where both gas and liquid form a homogeneous single phase. Thus, gaseous oxidants such as oxygen are completely miscible in supercritical water. As water density is lower, diffusivity and ion mobility are therefore higher. It is also well known that organic compounds are very soluble in this environment. Combined with the inherent high temperatures, these properties result in rapid oxidation of organic compounds without interfacial mass transfer limitations. SCWE can lead to complete destruction: organic carbon is converted into carbon dioxide, organic and inorganic nitrogen into nitrogen gas (N<sub>2</sub>), halogenated organics and inorganics into the corresponding acid, sulphonated organics and inorganics into sulphuric acid, metals are oxidised to their highest valency, and all volatile solids are destroyed.

The limitations were primarily due to relying on biomass as the sole source of fuel, despite the highly variable properties of biomass. The high moisture and ash contents in biomass fuels can cause ignition and combustion problems. The melting point of the dissolved ash can also be low which causes fouling and slagging problems. Because of the lower heating values of biomass accompanied by flame stability problems. It is anticipated that blending biomass with higher quality coal will reduce flame stability problems, as well as minimize corrosion effects. Biomass offers important advantages as a combustion feedstock due to the high volatility of the fuel and the high reactivity of both the fuel and the resulting char. However, it should be noticed that in comparison with solid fossil fuels, biomass contains much less carbon and more oxygen and has a low heating value, higher moisture content and lower density.

Sewage sludge, which is used in the experiments, was obtained from Petkim Petrochemical Complex Wastewater Treatment Plant. Sludge was a mixture of effluents of floatation sludge and biological sludge centrifuges. Organic matter rich activated sludge must

be converted into fuels or chemical feedstocks by the help of economical and environmentally friendly processes.

Since sewage sludges generally include heavy metals, organochlorines and pathogens, proper disposal methods must be selected. Mostly used disposal methods are landfilling, using in agriculture and incineration. The restriction in disposal sites and liberation of hazardous gases by incineration forced researchers to develop new methods to convert sewage sludge into valuable hydrocarbons. There are so many studies at present to convert sludge into chemicals and fuels by using gasification, pyrolysis and liquefaction. Supercritical water extraction of sewage sludge was not encountered in literature.

In this study, Soxhlet extraction of sewage sludge samples was carried out with different solvents for the selection of suitable solvents giving the maximum recovery of organic matter. Maximum values were reached by using Dichloromethane-Methanol mixture, acetic acid, THF and Toluene, as solvents. High recovery of organic matter was obtained by using solvents having similar functional groups with the hydrocarbon compounds in the sludge. Since the maximum total conversion of organic matter obtained by Soxhlet extraction of activated sludge with Dichloromethane-Methanol mixture was 31.52 wt.%, which was so low compared with the supercritical water and toluene extraction processes. In the following studies, extraction of activated sludge with water and toluene was performed at different solvent/solid ratios and temperatures. Initial experiments were carried out by changing solvent/solid ratios as 3, 1.5 and 1 at two selected temperatures, which were 400°C and 425°C. All experiments performed for 1 hour after reaching reaction temperature. Variation of product yields with solvent/solid ratio for SCWE and SCTE of activated sludge were given in Table 5.3 and 5.6, respectively. Also, total yield (extract and gas yield) and total conversion of organic matter was tabulated in Table 5.4 and Table 5.7 for SCWE and SCTE, respectively. If these values were compared, total product yield and total conversion of organic matter at different solvent/solid ratios were very closer to each other for SCWE and SCTE, separately. So, solvent/solid ratios were selected to be 1 for both of extraction processes. Also, total product yield and total conversion values were higher in SCWE than SCTE. For example, total conversion of organic matter was 81.38 wt.% for SCWE and 73.59 wt.% for SCTE, when reaction temperature was 400°C and solvent/solid ratio was 1. (Table 5.4 and 5.7)

After selection of solvent/solid ratio to be 1, reaction temperature was changed between 325-450°C for SCWE and 300-450°C for SCTE. Reactions were performed at subcritical and supercritical conditions to be able to compare the difference in product distribution. When solvent/solid ratio was 1, variation of product yields with temperature for SCWE and SCTE were tabulated in Table 5.9 and 5.11, respectively. Extract and gas product yields increased by increasing temperature and extract yield reached its maximum value (44.40 wt.%) at 425°C for SCWE. Also, extract and product yields increased by increasing temperature and extract yield reached its maximum value (44.97 wt.%) at 300°C for SCTE. The total product yields were higher in SCWE than SCTE at every reaction temperature (Figure 5.6 and 5.8). The total conversion was higher in SCWE than SCTE at every reaction temperature (Figure 5.9). After that, gas product distributions at different solvent/solid ratios and temperatures were analyzed by gas chromatographic systems at which extraction products ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$  and  $\text{C}_1\text{--C}_{6+}$ ) were identified.

In SCWE of activated sludge,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2$ ; in SCTE of activated sludge,  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{C}_2$  are the major products. Gas product distributions were investigated by changing solvent/solid ratio and temperature. Variations of gas product distribution for SCWE and SCTE of activated sludge with temperature were given in Table 5.20 and 5.24.

$\text{CO}_2$  and  $\text{CO}$  yields are indicators of the oxygen present in the sample in extraction processes. The oxygen present could originate from two different sources: decomposition of inorganic salts as carbonates (only at high temperatures) or from pyrolytic decomposition of partially oxygenated organic compounds such as cellulose, lignin, lipids or carbohydrates.

When the temperature increased from 350°C to 450°C for SCWE, amount of  $\text{CH}_4$  increased from 9.81 v.% to 18.07 v.%, amount of  $\text{CO}_2$  decreased from 56.70 v.% to 29.29 v.% and amount of  $\text{H}_2$  increased from 15.69 v.% to 26.44 v.% (Table 5.20). The increase in the amount of  $\text{CH}_4$  can be explained by conversion of high molecular weight hydrocarbons to low molecular weight hydrocarbons by thermal cracking mechanism. As the reaction temperature increases, the amount of  $\text{CO}_2$  decreased, which can be explained by absorption of  $\text{CO}_2$  as Calcium, Magnesium or Ammonium Bicarbonates. This situation was tried to be confirmed by measuring pH of the extraction products. The pH of extraction products was 8, which is closer to pH of mentioned Bicarbonate solutions. And the increase in the amount of

H<sub>2</sub> can be explained by thermal cracking of unsaturated hydrocarbons and aromatization of cyclic hydrocarbons.

Same experiments were performed by using toluene as extraction fluid. Temperature increased from 300°C to 450°C, it was found that amount of CH<sub>4</sub> increased from 22.85 v.% to 55.13 v.%, amounts of CO<sub>2</sub> decreased from 37.55 v.% to 22.65 v.% and amount of H<sub>2</sub> decreased from 12.03 v.% to 9.11 v.%.

After identification of gas product distribution, deasphalted oil products were fractionated into aliphatics, aromatics and polars by liquid absorption chromatography. Aliphatic fractions were analyzed by gas chromatography and separated into gasoline, middle distillates and wide cut gas-oil fractions according to their boiling points.

Aliphatic fractions of oil obtained from SCWE were given in Table 5.28 and it was realized that gasoline fractions decreased, middle distillates and wide cut gas-oil fractions increased when the temperature increased (Figure 5.26). These fractions were obtained by using simulated distillation curves (Figure 5.27). Also, aliphatic/aromatic ratios in deasphalted oil obtained from extraction with water were calculated by using spectroscopic analysis (IR). It was found that, aliphatic/aromatic ratio increased by increasing temperature (Table 5.29).

Aliphatic fractions of oil obtained from SCTE were given in Table 5.30 and it was realized that gasoline fractions increased, middle distillates and wide cut gas-oil fractions decreased when the temperature increased (Figure 5.28). These fractions were obtained by using simulated distillation curves (Figure 5.29). Also, aliphatic/aromatic ratios in deasphalted oil obtained from extraction with toluene were calculated by using spectroscopic analysis (IR). It was found that, aliphatic/aromatic ratio decreased by increasing temperature (Table 5.31).

## REFERENCES

- Boocock, G.B., Bahadur, N.P. and Konar, S. K.,** 1995, Liquid hydrocarbons from catalytic pyrolysis of sewage sludge lipid and canola oil: Evaluation of fuel properties, *Energy and Fuels*, 248-256p
- Ballice, L., and Larsen, J. W.,** 2003, Changes in the cross-link density of Goyunuk oil shale (Turkey) on pyrolysis, *Fuel*, 82, 1305–1310p
- Biosolids Generation,** 1999, Use and Disposal in the United States; U.S. Environmental Protection Agency, EPA530-R-99-009, Office of Solid Waste and Emergency Response: Washington, DC.
- Bridgewater, A. V.,** 1999, Principles and practice of biomass fast pyrolysis processes for liquids, *Journal of Analytical and Applied Pyrolysis*, 51, 3-22p
- Bridgewater, A. V. and Peacocke, G. V. C.,** 2000, Fast pyrolysis processes for biomass, *Renewable and sustainable energy reviews*, 4, 1-73p
- Bridgewater, A. V.,** 2003, Renewable fuels and chemicals by thermal processing of biomass, *Chemical Engineering Journal*, 91, 87-102p
- Bridgewater, A. V., Meier, D. and Raglein, D.,** 1999, An overview of fast pyrolysis of biomass, *Organic Geochemistry*, 30, 1479-1493p
- Caballero, J.A., Font, R., Marcilla, A. and Conesa, J. A.,** 1997, Characterization of sewage sludges by primary and secondary pyrolysis, *Journal of Analytical and Applied Pyrolysis*, 40-41, 433-450p

**Cabelli, V.J.**, 1983, Health effects of criteria for marine recreational waters, Pub. No. EPA-600/1-80-031, U.S. Environmental Protection Agency, Washington, D.C.

**Chao, C. G., Chiang, H. L. and Chen, C. Y.**, 2002, Pyrolytic kinetics of sludge from a petrochemical factory wastewater treatment plant-a transition state theory approach, *Chemosphere*, 49, 431-437p

**Conesa J. A., Marcilla, A. and Moral, R.**, 1998, Evaluation of gases in the primary pyrolysis of different sewage sludges, *Thermochimica Acta*, 313, 63-73p

**Degremont**, 1991, *Water Treatment Handbook*, 6<sup>th</sup> edition.

**Demirbaş, A.**, 2001, Supercritical fluid extraction and chemicals from biomass with supercritical fluids, *Energy Conversion and Management*, 42, 279-294p

**Eltem, R.**, 2001, Atık Sular ve Arıtımı, Ege Üniversitesi Fen Fakültesi Yayınları No:172.

**Fullana, A., Conesa, A. J. and Font, R.**, 2003, Pyrolysis of sewage sludge: nitrogenated compounds and pretreatment effects, *Journal of analytical and applied pyrolysis*, 68, 561-575p

**Hammer, M. J.**, 1996, *Water and Wastewater Technology*, 3<sup>rd</sup> edition.

**Inoue, S., Sawayama, S. and Dote., Y.**, 1997, Behaviour of nitrogen during liquefaction of dewatered sewage sludge, *Biomass and Bioenergy*, 12, 473-475p

**Kaminsky, W. and A. B. Kummer**, 1989, Fluidized bed pyrolysis of digested sewage sludge, *Journal of Analytical and Applied Pyrolysis*, 16, 1, 27-35p

- Konar, S. K., Boocock, D. G. B., Mao, V. and Liu, J.,** 1994, Fuels and chemicals from sewage sludge: 3. Hydrocarbon liquids from the catalytic pyrolysis of sewage sludge lipids over activated alumina, *Fuel*, 73, 642-646p
- Kuriakose, A.P. and Manjooran, S. K. B.,** 1994, Utilization of refinery sludge for lighter oils and industrial bitumen, *Energy and Fuels*, 788-792p
- Lin, J., Arunkumar, R., and Liu, C.,** 1999, Efficiency of supercritical fluid extraction for determining 4-nonylphenol in municipal sewage sludge, *Journal of Chromatography A*, 840, 71-79p
- Metcalf and Eddy,** 1991, *Wastewater Engineering: Treatment, Disposal and Reuse*, 3<sup>rd</sup> edition.
- Montgomery, J. M.,** 1986, *Water treatment principles and design*.
- Olukçu, N., Yanık, J. and Sağlam, M.,** 1999, Solvent effect on the extraction of Beypazari Oil Shale, *Energy and Fuels*, 13, 895-902p
- Özkan A.R., Yanık, J. and Sağlam, M.,** 1998, Catalytic upgrading of “Off-Spec” aromatic-rich oils from the NSC process, *Energy and Fuels*, 13, 433-439p
- Priestley, A. J.,** 1990, *Report on Sewage Sludge Treatment and Disposal -Environmental Problems and Research Needs From An Australian Perspective*, CSIRO, Division of Chemicals and Polymers.
- Punnaruttanakun, P., Meeyoo, V. and Kalambaheti, C.,** 2003, Pyrolysis of API separator sludge, *Journal of analytical and applied pyrolysis*, 68-69, 547-560p

**Rudzinski, W. E. and Aminabhavi, T. M.,** 1999, A Review on Extraction and Identification of Crude Oil and Related Products Using Supercritical Fluid Technology, Energy and Fuels, 14, 464-475p

**Rudzinski, W. E., Aminabhavi, T. M. and Sassman, S.,** 2000, Isolation and Characterization of the Saturate and Aromatic Fractions of a Maya Crude Oil, Energy & Fuels, 14, 839-844p

**Shen, L. and Zhang, D.,** 2003, An experimental study of oil recovery from sewage sludge by low-temperature pyrolysis in a fluidised-bed, Fuel, 82, 465-472p

**Tian, F., Li, B. and Chen., Y.,** 2002, Formation of NO<sub>x</sub> precursors during the pyrolysis of coal and biomass. Part V. Pyrolysis of a sewage sludge, Fuel, 83, 2203-2208p

**Weismantel, G. E.,** 1991, Chemical Engineering Applications in Solid Waste Management.

**Yokoyama, S., Suzuki, A. and Murakami, M.,** 1987, Liquid fuel production from sewage sludge by catalytic conversion using sodium carbonate, Fuel, 66, 1150-1155p

[www.die.gov.tr](http://www.die.gov.tr)

[www.petkim.gov.tr](http://www.petkim.gov.tr)

## APPENDIX

### I. Calculation of Heating Value of Sewage Sludge

0.8364 g of sewage sludge (moisture content and H content are 4.48% and 5.9%, respectively) was placed in a calorimetry bomb which includes 2 liters of water. 1.535°C of temperature change was occurred in water bath. 15 kcal/kg of energy was consumed during combustion of 10cm of iron wire that was connected between two electrodes.

#### a. Higher Heating Value (HHV) of Sewage Sludge:

$$Q_1 = \frac{2395 \times \Delta T}{\text{Weight of sample}} - 15 = \frac{2395 \times 1.535}{0.8364} - 15 = 4380 \frac{\text{kcal}}{\text{kg}} = 18308 \frac{\text{kJ}}{\text{kg}}$$

#### b. Lower Heating Value (LHV) of Sewage Sludge:

$$Q_2 = Q_1 - 6(9H + W)$$

$$Q_2 = 4380 - 6(9 \times 5.9 + 4.48) = 4034.5 \frac{\text{kcal}}{\text{kg}} = 16864 \frac{\text{kJ}}{\text{kg}}$$

### II. Calculation of Extract Yield and Total Conversion of Organic Matter in Sewage Sludge

#### Inputs of autoclave:

$M_{\text{sample}} = 10$  g of sewage sludge

$M_{\text{solvent}} = 10$  g of water

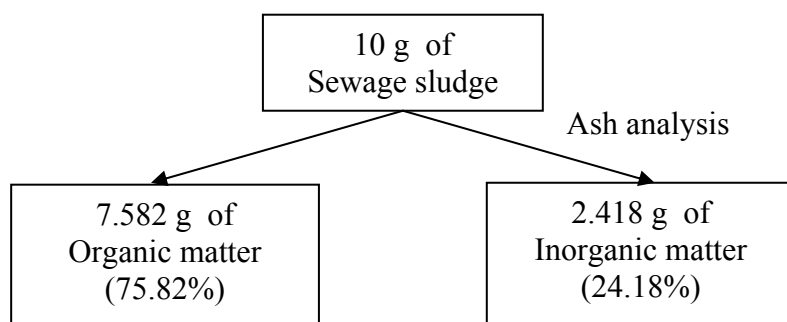
#### Outputs of autoclave:

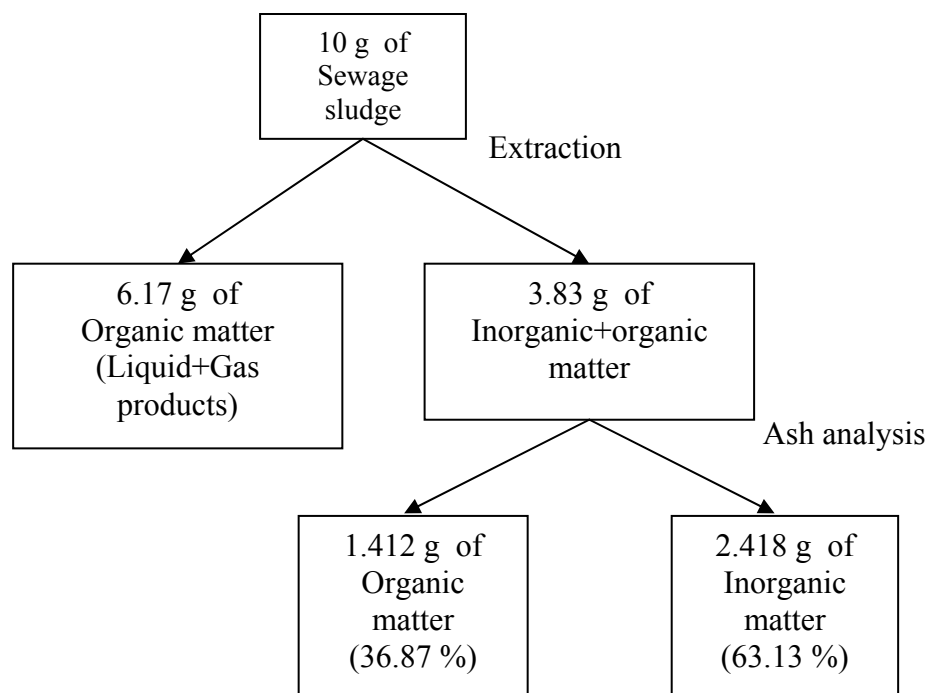
$M_{\text{residue}} = 3.83$  g

$M_{\text{gas product}} = 1.87$  g

$M_{\text{extract}} = 10 - (3.83 + 1.87) = 4.3$  g

According to ash analysis, sewage sludge sample consists of 75.18% organic matter. Also, ash analysis was applied to sewage sludge residue after supercritical fluid extraction to be able to calculate amount of dissolved organic matter.





#### a. Calculation of Extract Yield

$$\text{Extract Yield(\%)} = \frac{A}{B} \times 100$$

A: Weight of extract (d) (g)

B: Weight of sewage sludge (d) (g)

$$\text{Extract Yield(\%)} = \frac{4.30}{10} \times 100 = 43 \% \text{ (Table 5.3)}$$

#### b. Calculation of Total Conversion of Organic Matter

$$\text{Total Conversion of Organic Matter(\%)} = \frac{C - D}{C} \times 100$$

C: Organic matter content of sewage sludge (daf) (g)

D: Organic matter content of spent sewage sludge (daf) (g)

$$\text{Total Conversion of Organic Matter(\%)} = \frac{7.582 - 1.412}{7.582} \times 100 = 81.38\%$$

$$\text{Total Product Yield(\%)} = \text{Extract Yield} + \text{Gas Yield}$$

$$\text{Total Product Yield(\%)} = 43 + 18.7 = 61.70\% \text{ (Table 5.4)}$$

**c. Calculation of Extract Content**

Extract (%) = Oil (%) +Asphaltenes (%) + Preasphaltenes (%)

Weight of preasphaltenes= 0.0038 g

Weight of asphaltenes= 0.0322 g

Weight of extract= 4.3 g

Weight of oil= 4.3-(0.0038+0.0322) = 4.264 g

$$\text{Oil (\%)} = \frac{\text{Weight of oil}}{\text{Weight of sewage sludge}} \times 100 = \frac{4.264}{10} \times 100 = 42.64\%$$

$$\text{Asphaltenes (\%)} = \frac{\text{Weight of asphaltenes}}{\text{Weight of sewage sludge}} \times 100 = \frac{0.0322}{10} \times 100 = 0.322\%$$

$$\text{Preasphaltenes (\%)} = \frac{\text{Weight of preasphaltenes}}{\text{Weight of sewage sludge}} \times 100 = \frac{0.0038}{10} \times 100 = 0.038\%$$

$$\text{Extract (\%)} = 42.64(\%) + 0.322 (\%) + 0.038 (\%) = 43(\%)$$

**RESUME**

Tülay GÜNGÖREN was born in İzmit in 1980. She received BSc in Chemical Engineering Department from Engineering Faculty of Ege University in 2002.

She has been working as a research assistant in Chemical Engineering Department of Ege University since September 2002.

She completed her MSc Thesis which was “Investigation of Supercritical and Soxhlet Extractions of Sewage Sludges” in September 2004.