CONTENTS

| I | Page |
|---|------|
| CONTENTS | IX |
| LIST OF TABLES | XIII |
| LIST OF FIGURES | XV |
| CHAPTER I Introduction | 1 |
| 1.1 Rationale and background | 1 |
| 1.2 Thesis objectives | 4 |
| 1.3 Research scope | 5 |
| CHAPTER II Literature review | 6 |
| 2.1 Substrates used | 6 |
| 2.1.1 Skim latex serum | 6 |
| 2.1.1.1 Compositions of non-rubber materials in the serum | 6 |
| 2.1.1.1.1 Carbohydrates | 6 |
| 2.1.1.1.2 Proteins | 7 |
| 2.1.1.1.3 Lipids and phospholipids | 7 |
| 2.1.2 Palm oil mill effluent | 9 |
| 2.2 The biogas process | 12 |
| 2.2.1 Hydrolysis | 13 |
| 2.2.2 Acidogenesis | 14 |
| 2.2.3 Acetogenesis | 14 |
| 2.2.4 Methanogenesis | 14 |
| 2.3 Two-stage anaerobic digestion process | 15 |
| 2.4 Factors affecting the stability of the biogas production by dark fermentation | 16 |
| 2.4.1 Substrate | 16 |
| 2.4.2 Nutrients | 16 |
| 2.4.3 Operating conditions | 17 |

CONT

| CONTENTS (Continued) | | |
|--|------|--|
| | Page | |
| 2.4.3.1 Temperature | 17 | |
| 2.4.3.2 pH and buffers | 17 | |
| 2.4.3.3 Organic loading rate | 18 | |
| 2.4.3.4 Hydraulic retention time | 18 | |
| 2.4.4 Toxic/inhibiting compounds | 18 | |
| CHAPTER III Hydrogen and methane production by using batch two-stage | 21 | |
| co-digestion of skim latex serum (SLS) and palm oil mill | | |
| effluent (POME): Optimization of mixing ratio and nutrients | | |
| 3.1 Abstract | 21 | |
| 3.2 Introduction | 22 | |
| 3.3 Materials and methods | 23 | |
| 3.3.1 Anaerobic seed sludge | 23 | |
| 3.3.2 Skim latex serum | 24 | |
| 3.3.3 Palm oil mill effluent | 24 | |
| 3.3.4 Empty fruit bunch (EER) ash | 24 | |

| 3.3.4 Empty fruit bunch (EFB) ash | 24 |
|---|----|
| 3.3.5 Optimization of SLS and POME mixing ratio in biohydrogen | 25 |
| production | |
| 3.3.6 Effect of NaHCO ₃ , Na ₂ HPO ₄ .12H ₂ O and EFB ash | 25 |
| concentrations on biohydrogen production | |
| 3.3.7 Methane potential from co-digestion of SLS with POME | 27 |
| 3.3.8 Analytical methods | 28 |
| 3.4 Results and discussion | 28 |
| 3.4.1 Characteristics of substrates used | 28 |
| 3.4.2 Optimization of SLS and POME mixing ratio in biohydrogen | 29 |

Production

CONTENTS (Continued)

| | Page |
|--|------|
| 3.4.3 Effect of NaHCO ₃ , Na ₂ HPO ₄ .12H ₂ O and EFB ash concentrations | 33 |
| on biohydrogen production | |
| 3.4.4 Soluble metabolite products and COD balance | 36 |
| 3.4.5 Methane potential of co-fermentation of SLS and POME | 44 |
| 3.5 Conclusions | 46 |
| CHAPTER IV Thermophilic dark co-digestion of skim latex serum (SLS) and | 47 |
| palm oil mill effluent (POME) to sequentially produce hydrogen | |
| and methane | |
| 4.1 Abstract | 47 |
| 4.2 Introduction | 48 |
| 4.3 Materials and methods | 49 |
| 4.3.1 Inoculum preparation | 49 |
| 4.3.2 Skim latex serum | 50 |
| 4.3.3 Palm oil mill effluent | 50 |
| 4.3.4 Experimental set-up and operation | 51 |
| 4.3.5 Analytical methods | 53 |
| 4.4 Results and discussion | 53 |
| 4.4.1 H ₂ -CSTR experiments | 53 |
| 4.4.2 CH ₄ -UASB experiments | 58 |
| 4.4.3 Energy achieved from two-stage co-digestion of SLS with POME | 61 |
| 4.5 Conclusions | 62 |
| CHAPTER V Conclusions | 63 |
| 5.1 Summary | 63 |
| 5.2 Suggestions | 64 |
| REFERENCES | 65 |

CONTENTS (Continued)

| | Page |
|------------|------|
| APPENDICES | 72 |
| VITAE | 83 |



LIST OF TABLES

| | Page |
|--|----------|
| Table 2.1 Physical and chemical characteristics of skim latex serum | 8 |
| Table 2.2 Physical and chemical characteristics of palm oil mill effluent | 9 |
| Table 2.3 Hydrogen and methane production from anaerobic digestion | 10 |
| of POME under mesophilic and thermophilic conditions | |
| Table 3.1 Physical and chemical characteristics of skim latex serum and | 29 |
| palm oil mill effluent | |
| Table 3.2 Experimental variables and concentration levels investigated by using central composite design Table 3.3 Central composite experimental design matrix defining NaHCOa | 26 27 |
| Na. HPO, 12H.O and EEB ash concentrations on hydrogen production yield | 21 |
| Na211F 04.121120 and EFB ash concentrations on hydrogen production yield | |
| Table 3.4 Analysis of variance (ANOVA) for the regression modelTable 3.5 Model coefficients estimated by multiples linear regression | 35 35 |
| (significance of regression coefficients), where $X_1 = NaHCO_3$ concentration (g/L | L), |
| $X_2 = Na_2HPO_4.12H_2O$ concentration (mg/L) and $X_3 = EFB$ ash concentration (g/I | Ĺ) |
| Table 3.6 pH and results on hydrogen production yield achieved from buffer and macro- | 36 |
| nutrient optimization stage. | |
| Table 3.7 Soluble metabolites obtained from different mixing ratio of SLS to POME | 39 |
| with initial organic loading of 7 g-VS _{added} /L | |
| Table 3.8 Soluble metabolites obtained from different mixing ratio of SLS to POME | 41 |
| with initial organic loading of 21 g-VS _{added} /L | |
| Table 3.9 Soluble metabolite products and COD balance obtained from different | 43 |
| mixing ratio of SLS to POME with initial organic loading of 7 g-VS _{added} /L | |
| at the end of fermentation | |
| Table 3.10 Soluble metabolite products achieved from methane production in | 45 |
| batch experiment | |

LIST OF TABLES (Continued)

| | Page |
|---|------|
| Table 4.1 Physical and chemical characteristics of the skim latex serum and palm oil mill | 51 |
| effluent used | |



LIST OF FIGURES

Page

| Figure 1.1 Schematic diagram of research plan for hydrogen and methane production from co-digestion of skim latex serum and palm oil mill effluent under thermophilic condition | 5 |
|---|----|
| Figure 2.1 Process involved in concentration of natural latex using centrifugation method | 8 |
| Figure 2.2 Process involved in milling of oil palm | 12 |
| Figure 2.3 Carbon flow diagram of the biogas process | 13 |
| Figure 2.4 Flow diagram of two-stage anaerobic process | 15 |
| Figure 3.1 Cumulative hydrogen achieved from different mixing ratio of SLS and | 32 |
| POME with initial organic loading of 7 g-VS _{added} /L | |
| Figure 3.2 Cumulative hydrogen achieved from different mixing ratio of SLS and | 32 |
| POME with initial organic loading of 21 g-VS _{added} /L | |
| Figure 3.3 Hydrogen production yield achieved from different mixing ratio of SLS | 33 |
| and POME with initial organic loading of 7 g-VS _{added} /L and 21 g-VS _{added} /L, | |
| respectively | |
| Figure 3.4 Soluble metabolites obtained from different mixing ratio of SLS to POME | 38 |
| with initial organic loading of 7 g-VS _{added} /L | |
| Figure 3.5 Soluble metabolites obtained from different mixing ratio of SLS to POME | 41 |
| with initial organic loading of 21 g-VS _{added} /L | |
| Figure 3.6 Cumulative methane production achieved from the sequential methane | 44 |
| production in batch experiment | |
| Figure 3.7 Methane production yield achieved from the sequential methane production | 45 |
| in batch experiment | |
| Figure 4.1 Schematic description of lab-scale bioreactor operation for sequential production | 52 |
| of biohydrogen and biomethane which operated under thermophilic temperature | |

LIST OF FIGURES (Continued)

Page Figure 4.2 Variation of pH in H₂-CSTR reactor which was operated at different HRTs 56 under thermophilic temperatures; [1] HRT of 2.25 days and OLR of 20 g-VS/L d, [2,4] HRT of 4.50 days and OLR of 10 g-VS/L d, and [3] HRT of 4.50 days and OLR of 5 g-VS/L d Figure 4.3 Variation of hydrogen content in biogas at different HRTs achieved from 56 H2-CSTR reactor; [1] HRT of 2.25 days and OLR of 20 g-VS/L d, [2,4] HRT of 4.50 days and OLR of 10 g-VS/L d, and [3] HRT of 4.50 days and OLR of 5 g-VS/L d 57 Figure 4.4 H₂-CSTR reactor performance achieved from co-digestion of SLS to POME at different HRTs under thermophilic temperatures; [1] HRT of 2.25 days and OLR of 20 g-VS/L d, [2,4] HRT of 4.50 days and OLR of 10 g-VS/L d, and [3] HRT of 4.50 days and OLR of 5 g-VS/L d Figure 4.5 Variation of soluble metabolite products achieved from H₂-CSTR reactor 57 at different HRTs under thermophilic temperatures; [1] HRT of 2.25 days and OLR of 20 g-VS/L d, [2,4] HRT of 4.50 days and OLR of 10 g-VS/L d, and [3] HRT of 4.50 days and OLR of 5 g-VS/L d Figure 4.6 Variation of methane and carbon dioxide content achieved from CH₄-UASB 59 reactor at different HRTs under thermophilic temperatures; [1, 4] BA medium + sucrose 2 g/L, [2] (BA medium + sucrose 2 g/L) + effluent H₂ at 1:1 (%v/v), [3, 5, 7] BA medium + Effluent H₂ and [6] Effluent H₂ + NaHCO₃ 2 g/L Figure 4.7 Variation of soluble metabolite products achieved from CH₄-UASB reactor 60 at different HRTs under thermophilic temperatures; [1, 4] BA medium + sucrose 2 g/L, [2] (BA medium + sucrose 2 g/L) + effluent H₂ at 1:1 (%v/v), [3, 5, 7] BA medium + Effluent H₂ and [6] Effluent H₂ + NaHCO₃ 2 g/L

LIST OF FIGURES (Continued)

Page

61

60 Figure 4.8 Variation of methane production rate and methane production yield achieved from CH₄-UASB reactor at different HRTs under thermophilic temperatures; [1, 4] BA medium + sucrose 2 g/L, [2] (BA medium + sucrose 2 g/L) + effluent H₂ at 1:1 (%v/v), [3, 5, 7] BA medium + Effluent H₂ and [6] Effluent H₂ + NaHCO₃ 2 g/L

Figure 4.9 Variation of pH in CH₄-UASB reactor which was operated at different HRTs under thermophilic temperatures; [1, 4] BA medium + sucrose 2 g/L, [2] (BA medium + sucrose 2 g/L) + effluent H₂ at 1:1 (%v/v), Luent H2 + NaHC

[3, 5, 7] BA medium + Effluent H₂ and [6] Effluent H₂ + NaHCO₃ 2 g/L