ISTANBUL TECHNICAL UNIVERSITY ★ ENERGY INSTITUTE

OPERATION AND DEVELOPMENT OF AT-LINE CONTROL STRATEGY FOR THE BIOGAS PLANT IN HAMBURG

M.Sc. THESIS

Senem ÖNEN

Energy Science and Technology Division

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Thesis Advisor: Prof. Dr. Üner ÇOLAK

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ ENERJİ ENSTİTÜSÜ

HAMBURG'TA BİYOGAZ TESİSİ İŞLETİMİ VE AT-LINE KONTROL YÖNTEMİNİN GELİŞTİRİLMESİ

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To my family,

FOREWORD

This thesis was written in the Institute of Environmental Technology and Energy Economics (IUE) at Hamburg University of Technology (TUHH), in order to commit that thesis in the Institute of Energy at Istanbul Technical University (ITU). Researches were conducted both in biogas plant and in laboratory. The purpose of the research is to understand operation of biogas plant deeply and development of at-line control strategy for biogas plant.

Since October 2015 I have been conducting research on this topic with friendly host of IUE. First of all, I would like to express my deep gratitude to my IUE supervisor M. Sc. Iryna Atamaniuk for great guidance. She provided direction of my thesis with helpful ideas and technical support always in patient and willing way. My special thanks goes to M. Sc. Abdullah Nsair, his support was really helpful and lodestar.

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ABBREVIATIONS

AOTF	**:** Acousto-Optic Tunable Filter
Aq	**:** Aqua
CCD	**:** Charged Coupled Devices
DM	**:** Dry matter
EEG	**:** Renewable Energy Sources Act
FM	**:** Final Moistrue Content
FNR	**:** Fachagentur Nachwachsende Rohstoffe (Renewable Resources Agency)
FOS/TAC	**:** Flüchtige organische Säuren/ Totales anorganisches Carbonat (Volatile fatty acids/ Total inorganic carbonate)
InGaAs	**:** Indium gallium arsenite
LED	**:** Light Emitting Diodes
MSC	**:** Multiplicative Scatter Correlation
NH_3	**:** Ammonia
NH_4-N	**:** Ammonium nitrogen
NIR	**:** Near Infrared
oDM	**:** Organic dry matter
PbS	**:** Plumbum sulfide
PbSe	**:** Plumbum selenium
RMSECV	**:** Root Mean Square Error of Cross Validation
RMSEP	**:** Root Mean Square Error of Prediction.
RPD	**:** Ratio of Performance to Derivation
SBS	**:** Sugar Beets Sludge
SNV	**:** Standart Normal Variation
TKM	**:** Toplam Katı Madde
TN	**:** Total nitrogen
TUKM	**:** Toplam Uçucu Katı Madde
VFA	**:** Volatile fatty acids

SYMBOLS

h : Plank's constant
$H_{o,v}$: the calorific value
k : classical force constant
M : mass
Q : Heat generation
R : reflectance
T : transmittance
V : volume
ΔT : the temperature change
μ : reduced mass of two atoms
ν : vibration energy state
χ : anharmonicity constant of the vibration
ω : vibrational frequency

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OPERATION AND DEVELOPMENT OF AT-LINE CONTROL STRATEGY FOR THE BIOGAS PLANT IN HAMBURG

SUMMARY

Increased fossil fuel usage have affected all over the world and living organisms in negative way. Because of that, renewable energy had a good place in research areas about application of renewable energy. In order to find a solution to prevent climate change, biogas production by anaerobic digestion technology have been consideredas a new energy source. Application of anaerobic digestion technology offers new research oppurtunities to improve implementation in better way. Improving of on-line monitoring systems for biogas plants nowadays is significant topic. However, NIR spectroscopy is used as at-line controlling method, it is possible to integrate this system to biogas plant as an on-line monitoring method, which gives better monitoring oppurtunity. On the other hand, different kind of susbstrates have been used at biogas plants for years. With the aim of improving biogas production efficiency of biogas plants, new substrates usage in single way or as mixture is another topic to be improved.

This thesis rewievs general operation of a pilot scale biogas plant and development of NIR spectroscopy implementation as on-line monitoring system. Biogas plants monitoring was conducted with daily, weekly, monthly and yearly controls. Laboratory analyses were applied weekly to analyse DM, oDM, pH, FOS/TAC, NH_4-N, TN_{CD}, VFA and HCO_3^-. DM % increased from 1.57 % to 3 %; oDM % increased from 71.04 % to 76.88 %; pH value fluctated between 7.03 and 8.06; FOS/TAC increased from 0.132 to 1.73; NH_4-N concentration fluctated between 2921 mg/L and 4394 mg/L; range of TN_{CD} concentration was between 4.8 g/L – 6.8 g/L; concentration of VFA increased from 73 mg/L to 13865 mg/L; HCO_3^- concentration fluctated between 14985 mg/L and 20550 mg/L.

24 number of samples from biogas plant were used to improve calibration model for biogas plant monitoring parameters. Usability of parameters were evaluated depend on value of correlation coefficient (R^2) and value of Ratio of Performance to Derivation (RPD) . The results of calibration model are as follows; for DM 94.81 % R^2 and 4.39 % of RPD without pretreatment, for oDM 87.43 % R^2 and 2.82 % of RPD min-max normalaisation, for TN_{CD} 87.74 % R^2 and 2.86 % of RPD substraction of constant offsets, for VFA 87.16 % R^2 and 2.79 % of RPD min-max normalisation, for NH_4-N 84.26 % R^2 and 2.53 % of RPD multiplicative scatter and for HCO_3^- 70.74 % R^2 and 1.85 % of RPD min-max normalisation.

Based on previous researches, results were worth for biogas plant samples. It is necessary to continue further researches. In order to obtain better results, more samples should be included in analyses.

HAMBURG'TA BİYOGAZ TESİSİ İSLETİMİ VE AT-LINE KONTROL YÖNTEMİNİN GELİŞTİRİLMESİ

ÖZET

Fosil yakıtların kullanımının artması, zararlı gaz emisyonlarının artmasına sebep olmakta ve bütün dünyayı ve dünya üzerinde yaşayan canlıları olumsuz yönde etkilemektedir. Bu durum yenilenebilir enerji kaynaklarının kullanımının günden güne popüler olmasına sebep olmaktadır. Yenilenebilir enerji başlığı altında birçok teknoloji sıralanabilir. Anaerobik fermentasyon ile hiç atık üretmeden ve aynı zamanda biyolojik atıkların değerlendirilmesine olanak sağlayarak enerji üretilebilir. Küresel ısınmayı önlemek için çözüm olarak, anaerobik fermantasyon ile biyogaz üretimi uygulaması her geçen gün gelişmekte ve yaygınlaşmaktadır.

Anaerobik fermentasyon prosesi dört adımdan oluşur ve her basamakta farklı türde mikroorganizmalar görev almaktadır. Bundan dolayı her bir adımda görev alan mirrorganizmara uygun yaşamsal koşulların sağlanması gerekmektedir. Bir adımın ürünü diğer adımın hammaddesi olarak kullanılmakta ve proses sürekli olarak devam etmektedir. Herbir adımın birbirine bağlı olması, işletme koşullarını zorlaştırmaktadır. Herhangi bir adımda oluşabileek bir sorun, diğer adımları direk olarak etkilemekte ve prosesisin verimini düşürmekte ve hatta bazı durumlarda inhibe olmasına sebep olmaktadır.

Bu teknoloji geliştirilmesi gereken birçok konuyu da beraberinde getirir. Özellikle biyogaz tesislerinin işletilmesinde ve kontrol parametrelerinin takip edilmesinde sıkıntılar yaşanmaktadır. Almanya'da en ileri teknolojiler kullanımasına ve yaklaşık 9000 adet biyogaz tesisi olmasına rağmen, halen parametre takiplerinde problemler yaşanmaktadır. On-line işletim sistemlerinin geliştirilmesi bu sorunlara çözüm olarak önerilmektedir. Bu sayede, analiz sonuçları herhangi bir zaman kaybı olmaksızın öğrenilebilecektir. Daha verimli işletme koşullarını sağlamak için halihazırda labaratuvarda at-line kontrol methodu olarak kullanılabilen NIR (Near Infrared) spektroskopi, on-line olarak fermentere direk bağlantı ile kullanılabilir. Bu sayede, laboaratuvar analizlerinden maddi tasarruf ve zaman tasarrufu elde edilebilir. Türkiye'de ve dünyada biyogaz tesislerinde substrat olarak, bölge olanaklarına bağlı olarak, çok çeşitli susbstratlar kullanılmaktadır. Örneğin Türkiye'de yaygın olarak hayvansal atıklar, tarım bitki atıkları ve gıda endüstrisi atıkları substrat olarak kullanılmaktadır. Geliştirilmesi gereken bir diğer konu ise, yıllardır kullanılan çeşitli substrat ve substrat karışımlarından daha verimli biyogaz üretimi sağlamaktır. Bilindiği üzere, her substratın içeriği ve buna bağlı olarak biyogaz potansiyeli birbrinden farklıdır. NIR spektroskopi substrat değişimlerinin sebep olduğu, parametre değişimlerinin hızlı ve kolay bir şekilde takibini sağlayarak, proses işleyişine erken müdahale fırsatları sunmaktadır.

NIR sektroskopi ile analizler basit, hızlı, kimyasal madde kullanmaksızın ve numuneye herhangi bir etkide bulunmadan yürütülebilmektedir. Bu teknoloji ile

endüstride birçok proses verimli bir şekilde kontrol edilebilir. Özellikle gıda, petrokimya, ilaç ve çevre labaratuvarlarında günümüzde yaygın olarak kullanılmaktadır. Çalışma prensibi near-infrared alanda (800–2500 nm or 12500–4000 cm^{-1}) ışık absorbsiyonuna dayanmakadır. Sistem ışık kaynağı, monokramotör, numune ve dedektörden oluşmaktadır. Si, PbS, PbSe veya Indium gallium arsenite (InGaAs) dedktörler, farklı koşullara bağlı olarak kullanılabilir. NIR spektroskopi hem miktar hem de içerik analizleri yapma fırsatı sunmaktadır. Bu tezde, miktar analizi özelliğinden yararlanılmıştır. Analizlerin yürütülmesi için öncelikle örnekler test edilmeli, konsantrasyona aralığı belirlenmeli, spektralar toplanmalı, matematiksel kalibrasyon modeli gelirştirilmeli ve cihazın programı ile test sonuçları kontrol edilmelidir. Tüm bu adımların sonrasında, model bilinmeye numunelerin test sonuçlarının tahmini için kullanılabilir ve geliştirlebilir. Daha güvenilir sonuçlar elde etemek için çeşitli matematiksel ön arıtma modelleri kullanılabilir. Bunlar; sabit ofsetlerin çıkarılması, temel normalizasyon, standart normal değişiklik, min. – maks. normalizasyon, çoğaltıcı saçılım korelasyonu, ilk türev ve ikinci türev yöntemleri olarak sıralanır. Tüm bu ön arıtma yöntemleri ile ve ön arıtma yöntemi uygulamadan elde edilen sonuçlar karşılaştırılarak, en iyi yöntemle kalibrasyon modelleri kurulur.

Bu tezde, pilot ölçekte biyogaz tesisi işletimi ve NIR spektroskopi yönteminin on-line kontrol yöntemi olarak kullanılması araştırıldı. Tesis bileşenleri; reaktör, gaz depolama, reaktörün el ile besleme girişi, yüksek basınçtan koruma sistemi, numune alma vanası, gaz boru sistemi ve gaz numune alma vanası, reaktör karıştırma sistemi, reaktör pencereleri, gaz yakma bacası ve otomatik besleme sistemidir. Tesis işletilmeye başlamadan önce, kullanılan substratın biyogaz üretim potansiyeli, toplam kuru madde ve toplam uçucu kuru madde içeriği laboratuvarda test edildi. Bu sayede pilot ölçekte üretilebilinecek biyogaz kapasitesi ve karşılaşılabilecek problemeler belirlendi, substratın fermentere beslenme miktarı planlandı. Ayrıce substratın yakılmasıyla elde edilebilecek olan kalorifik değeri de analiz edildi. Buna bağlı olarak, substratı içien yakma ve fermentasyon proses verimleri labaratuvar ölçekte karşılaştırılabildi. Biyogaz tesisinde substrat olarak organik içeriğe sahip olan pelet kullanıldı. Fermentere besleme miktarı işletim süresince (120 gün) değiştirildi 2 kg'dan 4,5 kg'a arttırıldı. 1,5 m^3 hacimli fermenter mezofilik koşullarda (ortalama 40 °C) ve sürekli karıştırma yöntemi (her 30 dk'da 2 dk pedal karıştırma sistemi tarafından otomatik olarak karıştırılarak) işletildi.

Biyogaz tesisi işletimi süresince günlük, haftalık, aylık ve yıllık kontroller yapıldı. Haftalık olarak fermenterden numune alındı, TKM, TUKM, pH, FOS/TAC, NH_4-N, TN_{CD}, VFA ve HCO_3^- analizleri laboratuvarda yapıldı. TKM % 1.57 % ' den 3 % 'e yükseldi; TUKM % 71.04 % 'den 76.88 % 'e yükseldi; pH değeri 7.03 ve 8.06 arasında değişti; FOS/TAC 0,132'den 1,73'e yükseldi; NH_4-N konsantrasyonu 2921 mg/L ve 4394 mg/L arasında değişti; TN_{CD} konsantrasyon aralığı 4.8 g/L – 6.8 g/L arasındadır; VFA konsantrasyonu 73 mg/L'den 13865 mg/L'ye yükseldi; HCO_3^- konsantrasyonu 14985 mg/L ve 20550 mg/L arasında değişiklik gösterdi. Bunun yanısıra çevre sıcaklığı, fermenter sıcaklığı, fermenter basıncı, günlük gaz üretim hacmi ve günlük enerji tüketimi verileri günlük olarak takip edildi. Fermenter tarafından üretilen biyogazın içeriği haftada iki kez ölçüldü. Tesisin enerji üretimi bu verilere dayanarak hesaplandı. Çevre sıcaklık değişimlerine bağlı olarak, fermenterin enerji tüetimindeki değişiklikler takip edildi. Bunlara ek olarak, fermenter gaz basıncı, enerji tüketimi ve fermenter sıcaklığı saatlik olarak hafıza kartına kaydedildi, daha sonra bu bilgiler kullanılara günlük ortalama değerleri hesaplandı.

Daha önce de bahsedildiği gibi, Near Infrared (NIR) spektroskopi yöntemi, çevrimiçi tesis işletimini geliştirmek üzere kullanıldı. Pilot biyogaz tesisinden alınan 24 numune NIR spektroskopi ile biyogaz tesisi kontrol parametreleri için kalibrasyon modeli kurmak üzere kullanıldı. Bu sistemin çalışma prensibi daha önceden analiz edilmiş numunelerin labaratuvar sonuçlarını kullanarak, bir kalibrasyon modeli kurulmasına dayanmaktadır. Daha sonra bu kalibrasyon modeli sayesinde, labaratuvarda analize gerek duyulmaksızın bu parametrele kalibrasyon modeli sayesinde NIR spektroskopi tarafından güvenli bir şekilde tahmin edilebilir. Pilot biyogaz tesisi numunelerinde, TKM, TUKM, $TN_{CD,}$ VFA, NH_4-N ve HCO_3^- parametreleri için kalibrasyon modelleri kuruldu. Elde edilen sonuçlar optimize edilerek bazı kalibrasyon modellerinde çeşitli ön arıtma yöntemleri kullanıldı. Kullanılan ön arıtma yöntemleri; min. – maks. Normalizasyon, sabit ofsetlerin çıkarılması ve çarpımsal dağılımdır. Kurulan kalibrasyon modellerinin kullanılabilirliği, korelasyon katsayısı (R^2) ve performans sapma oranı (RPD) sonuçlarına bağlı olarak belirlendi. Kalibrasyon modeli kurulum sonuçları şöyledir; TKM 94.81 % R^2 ve 4.39 % RPD ön arıtmasız, TUKM 87.43 % R^2 ve 2.82 % RPD min.-maks. normalizasyon, TN_{CD} 87.74 % R^2 ve 2.86 % of RPD sabit ofsetlerin çıkarılması, VFA 87.16 % R^2 ve 2.79 % RPD min.-maks. normalizasyon, NH_4-N 84.26 % R^2 ve 2.53 % of RPD çarpımsal dağılım ve HCO_3^- 70.74 % R^2 ve 1.85 % of RPD min.-maks. normalizasyon. NIR spektroskopi ile tahmin edilen parametreler, aynı numuneler için laboratuvarda da analiz edildi ve sonuçlar karşılaştırıldı. Sonuçların arasındaki farklara bağlı olarak kalibrasyon modellerinin güvenilebilirliği teyit edildi.

Pilot tesisten alınan numunelerle yapılan çalışmanın yanısıra, büyük ölçekli biyogaz tesisinden de numuneler alınarak, ortak bir kalibrasyon modeli kurma amaçlandı. İki tesisten de eşit sayıda numune kullanılarak kalibrasyon modelleri oluşturuldu. Bu sayede tek bir kalibrasyon modeli iki tesisin de parametrelerinin NIR spektroskopi ile tahmininde kullanılabilir. Bu çalışmanın sonunda, TKM, TUKM ve HCO_3^- için iki tesisin de numuneleri için kullanılabilecek kalibrasyon modelleri kuruldu. . Kalibrasyon modeli kurulum sonuçları şöyledir; TKM 90.04 % R^2 ve 3.18 % RPD çarpımsal dağılım, TUKM 80.98 % R^2 ve 1.28 % RPD ön arıtmasız ve HCO_3^- 81.15 % R^2 ve 2.3 % of RPD çarpımsal dağılım. Tekli ve çoklu kalibrasyon modellerinin güvenilirliğini araştırmak üzere, pilot biyogaz tesisi numunesi labaratuvar analiz sonuçları ile NIR spektroskopi tahminleri karşılaştırıldı. Farklı parametreler için, her iki kalibrasyo modeli ile de güvenilir sonuçlar gözlendi. Daha fazla parametre için kalibrasyon modeli her iki tesisten de daha fazla numune kullanılarak elde edilebilir. Hatta bu çalışmaya başka tesis bilgileri de eklenerek birkaç tesis için tek bir çoklu kalibrasyon modeli kurulabilir.

Propiyonik ve asetik asidin NIR spektroskopi ile on- line kontrolü için daha önce yapılan çalışmaya dayanarak, NIR spektrometer fermentere optik fiber ve sensör yardımıyla bağlanabilir. Bu sayede numune alım, labaratuvar analizi vb. konularda iş yükü azaltılır ve herhangi bir kimyasal madde tüketimi olmadan hızlı, kolay ve güvenilir bir şekilde kontrol parametreleri analizleri yürütülebilir.

İleride araştırma önerisi olarak, günümüzde biyogaz tesislerinde substrat olarak kullanılan şeker pancarı atıklarının, pilot ölçekteki biyogaz tesisinde de kullanılması verildi. Bu araştırmaya ilk adım olarak şeker pancarının biyogaz üretim potansiyeli labaratuvarda 21 gün süren deney çalışması ile belirlendi. Sonuçların tez süresince substrat olarak kullanılan peletlerin biyogaz üretim potansiyeline oldukça yakın olduğu gözlendi. Şeker pancarının su içeriği peletlere göre daha yüksek olduğundan, depolama koşullarının peletlere göre daha gelişmiş olması gerekmektedir. Toplam

kuru madde içeriğine bakılarak, peletlerin daha yüksek biyogaz içeriğine sahip olduğu, toplam uçucu kuru madde içeriğine bağlı olarak ta şeker pancarı atıklarının daha yüksek biyogaz potansiyeline sahip olduğu gözlendi.

Daha önce yapılan çalışmalara bağlı olarak, elde edilen alibrasyon modeli kurulumu sonuçlarının biyogaz tesisine uygun olduğu gözlenmiştir. Sonuçları geliştirmek ve daha güvenilir hale getirmek için numune sayısı arttırılırak ve/ veya farklı tesislerin analiz sonuçları ile de çalışmaya devam edilebilir.

1. INTRODUCTION

Worlds energy demand is mostly provided by fossil fuels. 50 % of global anthropogenic emissions of greenhouse gases produced by fossil fuel combustion[1]. According to Shell, world energy demand will increase 7 times until 2100 [2]. It is estimated by Shell that in 2050 renewable energy sources will provide 50% of world energy demand [2] .With the aim of reducing the green gas emissions and fossil fuel consumption, biogas production is considered as renewable energy solution. According to European Biogas Association Report 2014, the total number of biogas plants in Europa is 17 240 with 8 293 MW_{el} total installed capacity [3]. After the Renewable Energy Sources Act (EEG) came into force in 2000, the rate of production and utilization of biogas have increased [4] . In Table below (Table 1.1) the number of biogas plants in Germany states is shown.

Table 1.1: Number of biogas plants in Germany States 2014 [5].

State	Number of biogas plants
Bayern	2360
Niedersachsen	1562
Nordhein-Westfalen	1076
Baden-Würtemberg	893
Schleswig-Holstein	711
Mecklenburg-Vorpommern	511
Brandenburg	384
Sachsen-Anhalt	322
Thüringn	272
Sachsen	270
Hessen	198
Rheinland-Pfalz	149
Saarland	15
Hamburg	2
Berlin	1
Bremen	0

In Turkey, after Renewable Energy Law No.5346 on Utilization of Renewable Energy Resources for the Purpose of Generating Electrical Energy came into force in

2005, the investments of renewable energy has increased. The majority of biogas plants are located in eastern part of Turkey. The total installed number of biogas plants is 36 with 111.23 MW_{el} capacity[5]. In Table below (Table 1.2) the number and spesification of biogas plants in are presented with information os status, sectors and capacities [5].

Table 1.2: Overview of Biogas Plants in Turkey.

	Biogas Plants in operation	**Capacity in operation [MW]**	**Biogas Plants in planning**	**Capacity in planning [MW]**	**Biogas Plants total**	**Total Capacity [MW]**
Agriculture (animal waste, crops)	2	0.68	12	11.99	14	12.58
Food Industry (wastewater, organic waste)	17	13.68	2	3.88	19	17.56
Municipality (landfill gas, waste water)	17	96.98	12	34.72	29	131.70
Municipality (landfill gas)	13	93.04	9	32.03	22	125.08
Municipality (wastewater)	4	3.94	3	2.69	7	6.62
Undifined	0	0	23	61,16	23	61,16
Total	36	111,23	49	111,76	85	222,99

Biogas production process takes place in anaerobic conditions. In this process organic materials are broken down to biogas. Anaerobic decomposition process takes place naturally in nature components [4]. Human made fermentation processes can be designed in mesophilic conditions (25-40°C) or thermophilic conditions (50-55°C) [6]. The gas product consists of methane (50-75 vol. %) and carbon dioxide (25-50 vol. %). In addition, biogas also includes trace amounts of hydrogen, hydrogen sulphide, ammonia and other gases. Schematic representation of anaerobic digestion is shown in Figure 1.1.

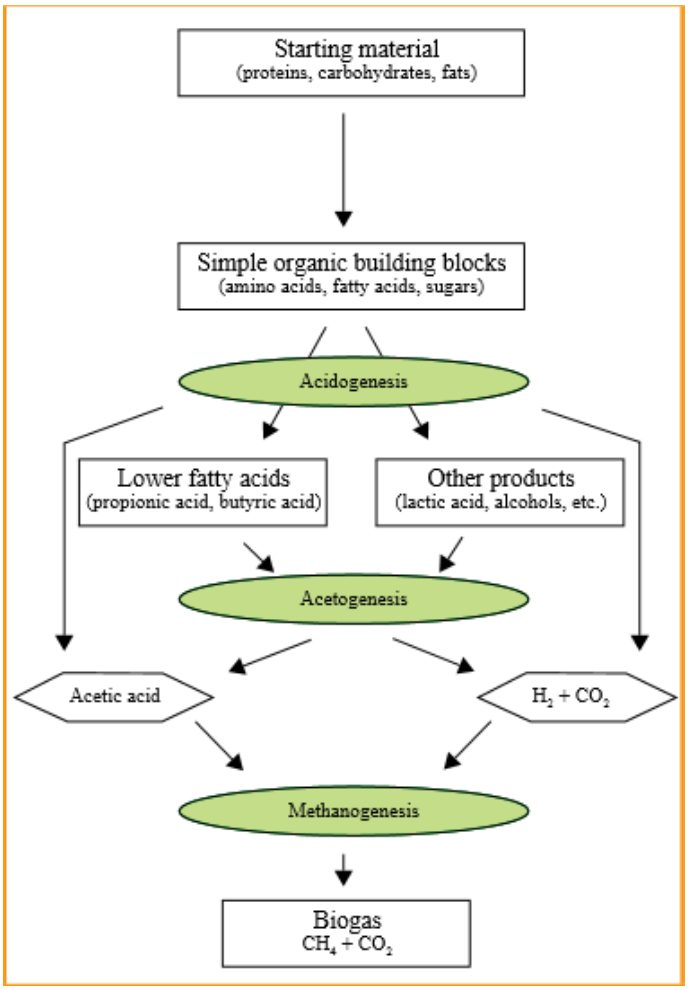

Figure 1.1: Anaerobic digestion proccess [4].

As can be seen, anaerobic digestion process consists of four steps; hydrolysis, acidogenis, acetogenis and methanogenesis. These four different fermentation steps are performend by different kind of bacterias[7].

1.1. Purpose of Thesis

The main objectives of this study can be summarized as followings:

- Biogas plant operation and development of the control strategy of the fermentation process by means of the temperature, pressure, substrate type and amount, energy consumption and daily biogas production volume.
- Monitoring of the most important parameters of the fermentation process such as: DM, oDM, pH, TN_{CD}, FOS/TAC, VFA, HCO_3^-, NH_4-N, biogas formation potential (GB_{21} test) and biogas composition.

- Development of the at-line control strategy of the fermentation process using NIR spectroscopy for analsing DM, oDM, TN_{CD}, VFA, HCO_3^- and NH_4-N.
- By means of statistic parameters to give a qualitative characterization of obtained model and specify the influence of different spectral pretreatment methods on correlation coefficient R^2, Root Mean Square Error of Cross Validation (RMSECV), bias and Ratio of Performance to Derivation (RPD).
- Based on obtained results give a further recommedations toward the on-line control strategy as well as the possibility of the substrate substitution.

1.2. Process Mechanism of Anaerobic Digestion

The anaerobic digestion process consists of four stages, which are hydrolysis, acidogenis, acetogenis and methanogenesis. In every stage, different chemical reactions occur. For efficient digestion process, every stage should have same degradation rate. If there is an inhibition in the first stages, there is not enough substrate, and biogas production efficiency will decrease. The inhibition in third stage can cause increasing acid concentration. The consequent of that inhibition is an inhibition of all processes. The different groups of bacteria, which are used for the fermentation process, supply substrate to next stages bacterias [8].

The critical fermentation stages and chemical reactions are explained below:

Hydrolysis stage: The substrate consists of complex mollecules. In order to break large compounds to small particles, water is used in hydrolysis stage. It happens with chemical bond breaking. This stage is performed by hydrolytic bacterias (facultative anaerobic or anaerobic) [8].

Hydrolysis stage conversions [8]:

Complex carbohydrates → Simple sugars

Complex lipids → Fatty acids

Complex proteins → Amino acids

Acidogenis stage: After hydrolysis stage, soluble components are degreded by facultative anaerobes and anaerobes. The result of degradation process is production of carbon dioxide, hydrogen gas, alcohols, organic acids, some organic-nitrogen compounds, and some organic-sulfur compounds [8].

Mean conversions in acidogenis stage:

Simple sugars + fatty acids + amino acids → organic acids, including acetate + alcohols

Acetogenesis stage: Many of acids and alcohols, which are produced in acidogenis process, are degraded to acetate. Acetate is used by methane-forming bacterias as a substrate to produce methane. Carbondioxide and hydrogen are directly transformed to methane by fermentative bacteria [8].

Organic acids + alcohols → acetate

Methanogenesis stage: In this stage, methane is formed mainly from acetate carbondioxide, hydrogen gas and some organic conpounds. All other fermentative products should be converted to compounds that can be in usable form by methanogenesis bacterias [8]

Acetoclastic methanogenesis:

$$\text{Acetate} \rightarrow CO_2 + CH_4$$

Hydogenotrophic methanogenesis:

$$H_2 + CO_2 \rightarrow CH_4$$

Methyltrophic methanogenesis:

$$\text{Methanol} \rightarrow CH_4 + H_2O$$

1.3. Biogas Production Bacterias

1.3.1. Acetate forming bacteria

Acetate forming bacterias (Acetogenic bacterias) survive in fermenter in symbiotic relationship with methane forming bacteria. The relationship caused from substrate supply to methane forming bacterias from acetate forming bacterias. The products of acetate forming reaction are acetate and hydrogen. In order to produce acetate from ethanol (CH_3CH_2OH) , acetate forming bacteria use CO_2 as a of carbon (C) and oxygen (O).

$$CH_3CH_2OH + CO_2 \rightarrow CH_3COOH + 2H_2$$

As a result of hydrogen accumulation, the reactor pressure can increase. But, in the methane formation reaction, H_2 is used for methane forming [8].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

1.3.2. Sulphate reducing bacteria

When sulphate prasens in anaerobic reactor, sulfate reducing bacteria multiply. Hydrogen and acetate are used as substrate by sulfate reducing bacterias. Hydrogen is used for reducing sulfate to hydrogen sulfate [8].

1.3.3. Methane forming bacteria

There are many different types of methane forming bacterias in anaerobic fermentation process. Altough, they have different fatures, they take part to methane production process. Types of methane forming bacterias with different substrate usage [8]:

1. Hydrogenotrophic methanogens: $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
2. Acetotrophic methanogens: $4CH_3COOH \rightarrow 4CO_2 + 2\ H_2$
   $4CO + 2H_2O \rightarrow CH_4 + 3CO_2$
3. Methylotrophic methanogens: $3CH_3COH + 6H \rightarrow 3CH_4 + 3H_2O$
   $4(CH_3)_3 - N + 6H_2O \rightarrow 9CH_4 + 3CO_2 + 4NH_3$

1.4. Effective Parameters on Fermantation Stability

For the purpose of avoiding instabilities in biogas operation, many of operation parameters should be taken in consideration. Priority operation proposals can be summarized as follows [9]:

- Continuous feeding rate
- Continuous feedstock mix
- If appropriated, gradual and careful change of feedstock mixes
- Stable temperature
- Constant stirring
- Continuous process monitoring and control

1.4.1. Variable feeding loads and intervals

This part can be classified into three categories as unstable feeding, organic overload and hydraulic overload.

Unstable feeding: Although it has not got major influence on process stability, it affects the biogas production rate. Unstable substrate mixture or unstable amount of feeding during the operation time can affect the biogas production rate.

Organic overload: If the amount of fed organic matter exceeds the total degradation capacity of microorganisms, organic overload occurs. Excess organic matter converts to volatile fatty acids (VFA), after that it accumulates in reactor. When VFA exceeds the buffer capacity, the pHdecreases.

Hydraulic overload: As organic overload, hydraulic overload affects also process stability negatively. If the hydraulic retention time is not enough to multiplication of anaerobic microorganisms, they can be washed out. As a result, VFA accumulate in reactor and acidifying microbes grow faster than methanogens. That leads to decreasing of biogas production [9].

1.4.2. Temperature changes

As known in general, the rising temperature causes to increasing of rate of reaction. Depend on organic structure, there is an optimum temperature in biological reactions. It is necessary to divide anaerobic process into two temperature ranges [4]:

- mesophilic range approx. 37 to 43°C
- thermophilic range approx. 50 to 60°C .

The daily temperature fluctations should be <1°C in thermophilic proccess, and 2-3 °C in mesophilic proccess [9]. For the feeding, substrate should be heated up temperature of the fermenter [4]**.** In addtion , for the start up of biogas plant the inoculum should be heated up to the operation temperature of fermnter[9]. In order to control possible temperature changes, the temperature sensors should be installed at various hights and also in dead zones [4]**.**

1.4.3. Ammonia inhibition

After the break down process of organic substances which contain nitrogen, they are converted into ammonia (NH_3) which is further is transformed to ammonium. Although nitrogen is vital nutrient for cells, the high concentrations of ammonia/ammonium causes to inhibition of methagonesis proccess[4]. Depending on the researches about ammonia inhibition, the various ammonium inhibitory concentrations are given [9]. According to FNR [4], ammonium inhibiton is given in percentage with the effect of concentration of NH_3-N at two different temperature (30°C and 38°C). As seen in Figure 1.2, the ammonium inhibition is higher at 38°C. The inhibition starts after NH_3-N concentration reaches around 30 mg/L at 38°C. For 30°C, the inhibition starting concentration is 40 mg/l NH_3-N [4].

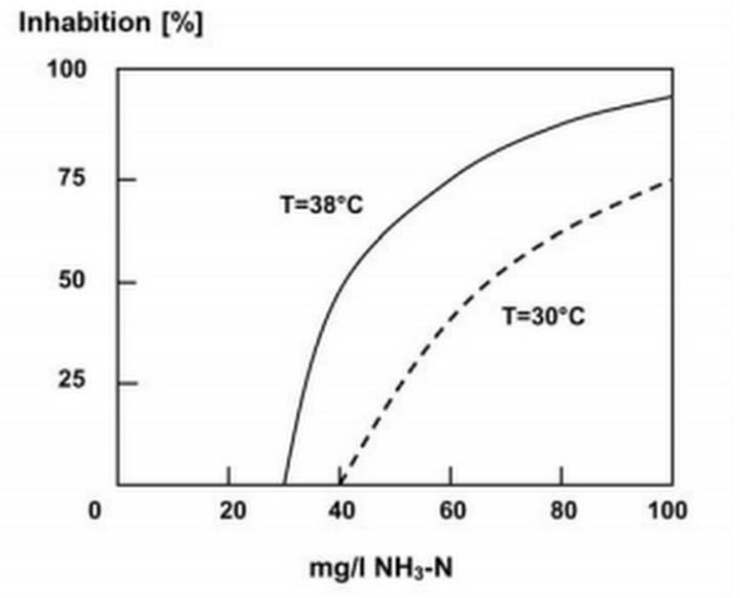

Figure 1.2: Ammonium inhibiton percentage affected from ammonium concentration and temperature [4].

1.4.4. Hyrdogen sulphide inhibition

The sulphur compounds convert to hyrdrogen sulphide (H_2S) with anaerobic degredation process. The undissociated form of free hyrdrogen sulphide (H_2S) has inhibitory effect on the fermentation process. On the other hand, hyrdrogen sulphide (H_2S) precipitates many metal ions which can have negative effect on the bioavailability of trace elements. The concentration of H_2S can be predicted by using the concentration of H_2S in the gas phase. According to Speece, 1% H_2S (10,000 ppm) in the gas phase corresponds to 26 mg H_2S (aq)L^{-1} at 35°C and a pH of 6,9 [10].

1.4.5. Other inhibitory substances

Heavy metal ions: Although the low concentrations of heavy metals are necessary to microbial activity, high concentrations can cause to toxic effect on microbial activity. The lover concentrations are tolerable in fermenter, but the heavy metal concentration of feedstock should be controlled [4].

1.4.5.1. Antibiotics and disinfectants

Antibiotics can be found in manure or other animal residue. That kind of compounds causes to inhibition of anaerobic microorganisms in fermentation process. Disinfectants are mostly used on farms or in the food industry. It is recommended

that the concentration of disinfectants should not be higher than recommended value for the farming. For the disinfectants, they should have low toxicity [4].

1.4.5.2. Trace elements

Trace elements are necessary for building up process of enzymes. Ni, Co, Mb, Se, Fe are necessary trace elements for the biological process. The scarcity of trace elements can lead to inhibition of the degradation process [4]. The recommended values of trace elements are given in Table 1.3.

Table 1.3: Recommended concentrations for trace elements [4].

Element	Guide values mg/kgDM	Guide values mg/L
Cobalt	0,4-10 (optimum 1,8)	0,06
Molybdenum	0,05-4 (optimum 4)	0,05
Nickel	4-30 (optimum 16)	0,006
Selenium	0,05-4 (optimum0,5)	0,008
Tungsten	0,1-30 (optimum 0,6)	-
Zinc	30-400 (optimum 200)	-
Manganase	100-1500 (optimum 300)	0,005-50
Copper	10-80 (optimum 40)	-
Iron	750-5000 (optimum 2400)	1-50

1.5. NIR Spectroscopy

1.5.1. General information

The Near Infrared (NIR) Spectroscopy is an analyzing technology that is simple, quick and nondestructive. The other advantage of this technology is there is no need to prepare samples with hazardous chemicals. This technology presents good opportunity for the controlling and monitoring various industrial processes [11] .

Nevertheless, NIR spectroscopy was discovered by William Herschel in 1800s, the usage of NIR technology was not getting common in these years. In 1980s, when this technology became more developed and accessible, it started to be use at industrial applications [12]. Starting from that days, the sectors which are use NIR technology are agricultural, food, pethrochemical, pharmaceutical, clinical, environmental and miscellaneous [13] . The theory of NIR spectroscopy can be explained as followings. It is based on absorption measured in the near-infrared region of the electromagnetic spectrum (800–2500 nm or 12500–4000 cm^{-1}). This technology is useful to study on vibrational properties of a sample. Intense absorbtion from molecular vibrations seems generally 400-4000 cm^{-1} wawelength. As can be seen in Figure 1.3,NIR region be located between visible and mid infrared region [13].

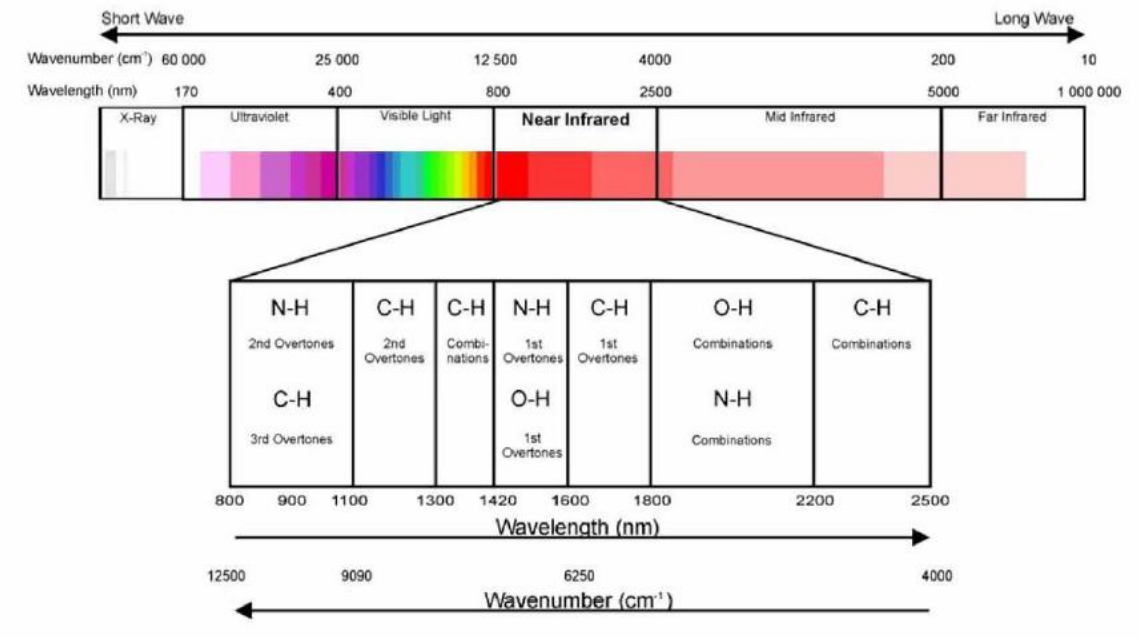

Figure 1.3: Electromagnetic spectrum with NIR region highlighted [13].

Based on the quantum theory, each atom and molecule has lowest energy state with named ground state. If they change their energy with the effect from radiation to higher states (overtone), the radiation is absorbed. Depend on absorbed energy, the vibrations take place. When the molecule returns to ground level, the photon is emitted. NIR absorbance spectrum can be seemed in energy absorbance time by atom or molecule [13]. The levels of NIR bands are shown in Figure 1.4.

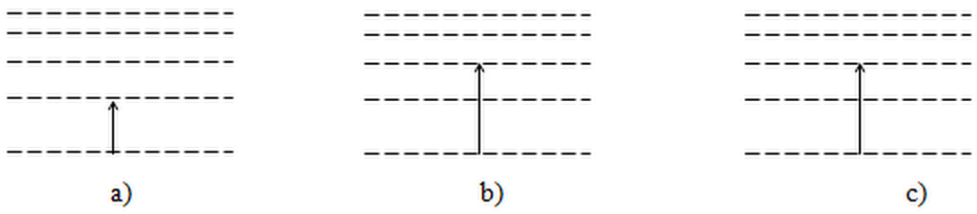

Figure 1.4: Energy levels for ground and overtone NIR bands; a) Ground level band, b) 1st overtone, c) 2nd overtone [12].

There are a few types of bond vibrations: Stretching vibrations,bending vibrations, fundamental band, overtones and combinations bands [13]. The molecular vibrations can be explained by combination of Hook`s law and Newton´s force law as shown in Equation (1.1).

$$\omega = \frac{1}{2\pi}\sqrt{k/\mu} \tag{1.1}$$

where ω is vibrational frequency, k is classical force constant, μ is reduced mass of two atoms [12].

Vibrational frequency gives information about samples structure and bond strength [11]. The implementation of harmonic oscillator model is limited. Because of the repulsion forces between vibrating atoms and probability of bond breaks when the dissociation energy is reached. For this reason, the anharmonic oscilation has supremacy usage. As is shown in Figure below (Figure 1.5), anhormonic oscillators have not stable energy difference between two energy levels.

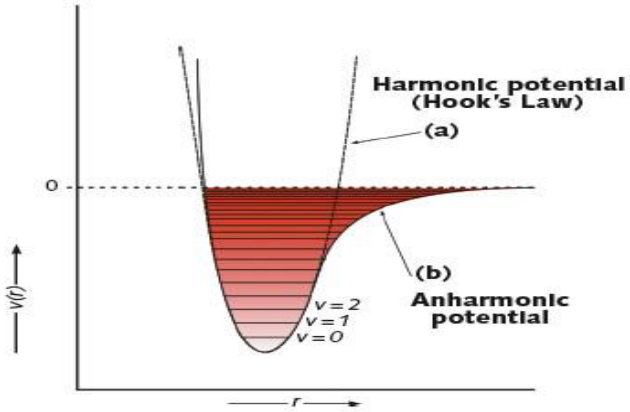

Figure 1.5: Energy diagram of ideal and anharmonic diatomic oscillators**[**12**]**.

In Equation 1.2, it can be explained with application of quantum theory.

$$E\upsilon = (\upsilon + 1/2)h\omega - (\upsilon + 1/2)^2 \times \omega + higherterms \quad (1.2)$$

where ω is vibrational frequency according to equation, ν is vibration energy state (ν = 0,1,2), χ is anharmonicity constant of the vibration (χ = 0.005-0.05), h is Plank's constant (h = $6.62 \cdot 10^{-34}$ $m^2 \cdot kg/s$).

1.5.2. Instrumentation

As shown in figure below (Figure 1.6), generally NIR instruments consist of monochromator, light source,detector and sample holder or sample presentation interface. But there are also some characteristic differences between NIR technologies [12].

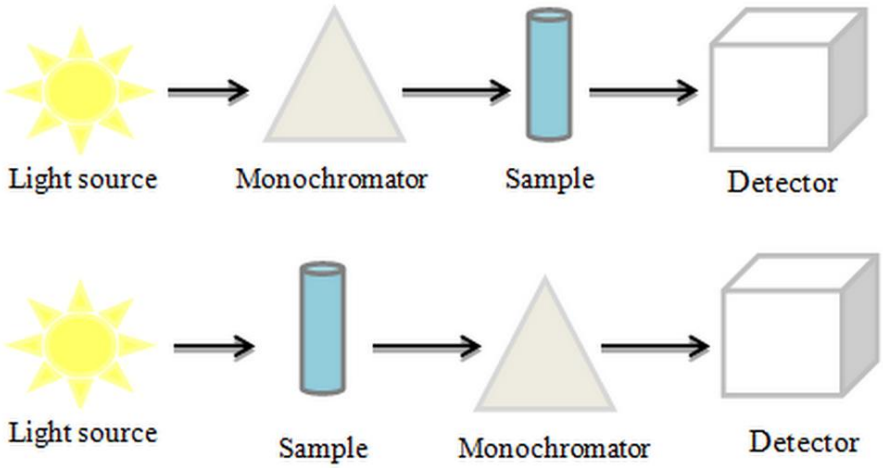

Figure 1.6: NIR Spectroscopy instrumentation**[**12**]**.

Depending on economic reasons and desirable characteristics, the dedectors can be made from Si, PbS, PbSe or Indium gallium arsenite (InGaAs) photoconductors [12]. The characteristics of dedectors are shown in Table 1.4.

Table 1.4: The characteristics of different kinds of NIR dedectors [12].

Material	Operational wavelength range, nm	Operational region	Speed of response	Selectivity
Si	780…1,100	UV-NIR	High	Medium
PbS	1,100…2,500	NIR		
	400…2,600	UV-NIR	Medium	Medium
	1,100…4,500	NIR-MIR		
PbSe	1,100...5,000	NIR-MIR	High	High
InGaAs	700...1,700	NIR	High	Very high
		NIR Raman		
InSb/InAs	1,000...5,500	NIR	High	Very high
		MIR		
		IR		
CCD	800...2,200	NIR	High	High

In terms of the technology employed for wavelength selection, the classification of NIR technologies are shown in Table 1.5.

Table 1.5: Classification of NIR technologies depend on wavelength selection technology [14].

I	Filter Instruments - Fabri-Perot (Interference); - Acousto-Optic Tunable Filter (AOTF)
II	LED source self-band selection instruments
III	Dispersive - Single beam; - Dual beam; - Multichannel (Detector array) - Multiplexed (Hadamard)
IV	Interferometric (Fourier-transform)

Filter based instruments filters are used as wavelength selectors and they are available for applications. However, filter based instruments have an extensive availability, and these instruments are not deeply discreibed in literature. For instance, A two25 and three26 filter-based instruments which have been described recently, are used for identification of polymers for recycling purposes and for the determination of proteins and nitrogen. That kind of examples prove the capability of instrument in high demand situations [14].

LED based instruments section; Light Emitting Diodes (LED) supplies low price and small size for instrumentation. In spectral region, they can produce NIR radiation with around 30-50 nm band width. The instruments can be used for producing narrow bands of near infrared radiation or polychromatic [14].

The instruments with Acousto-Optical Tunable Filters (AOTF)33 are defined as modern scan spectrophotometers and they supply a technology that allows constructing instruments with no moving parts. That kind of instruments can reach high scan speeds over a broad range of the NIR spectral region. In necessarry cases, the random access to any number of wavelengths is available. As shown in Figure below (Figure 1.7), the AOTF works in non-collinear configuration. For NIR Regions, TeO 2 is used as a main material in devices construction.

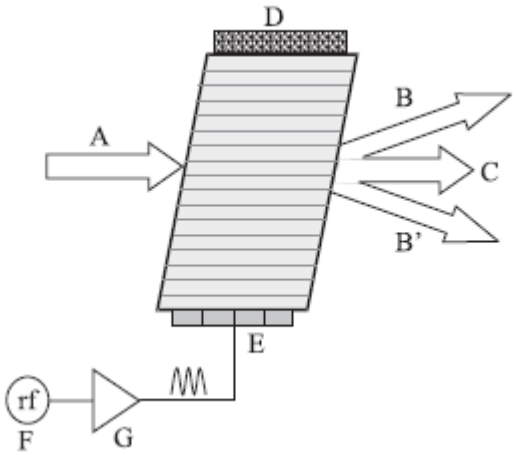

Figure 1.7: AOTF based intruments [14].

A- incident polychromatic radiation; B and B'- monochromatic beams (same wavelength); C - remaining polychromatic radiation; D - acousto absorber; E - piezoelectric transducer; F - generator of radio-frequency signal; G - radio frequency amplifier.

Early on development of NIR spectroscopy, dispersive instruments were used. This tchnology based on diffraction gratings. Compare with other technologies, they have relatively low costs. On the other hand, they have slow scan speed and a lack of wavelength precision. Because of this reason, it is possible that these instruments can not work for a long time. But, under favour of recent evolution in sensor production technology, the dispers optics can have longer life [14].

Spectrophotometers based on the use of interferometers and Fourier transform, they recover the intensities of individual wavelengths in the NIR region. In addition, they supply wavelength precision and accuracy, high signal-to-noise ratio and scan speed. But Fourier-transform based instruments are not fast as AOTF based instruments. As mentioned before, AOTF based intruments have high durableness. There are also kind of Fourier spectrophometes, which have durability under development by using a "wishbone" type of interferometer. The Bomen instruments is shown in Figure below (Figure 1.8), "wishbone" interferometric system employed in NIR spectrometers based on Fourier Transform.

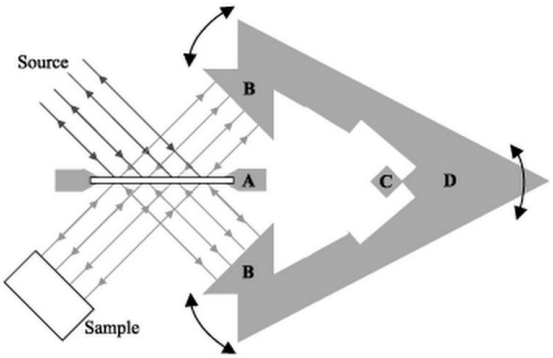

Figure 1.8: Fourier-transform based instruments; A, beam splilter; B, corner cubic mirrors; C, anshor; D, wishbone [14].

The general wiev of NIR instrumentation are summarized in Figure 1.9.

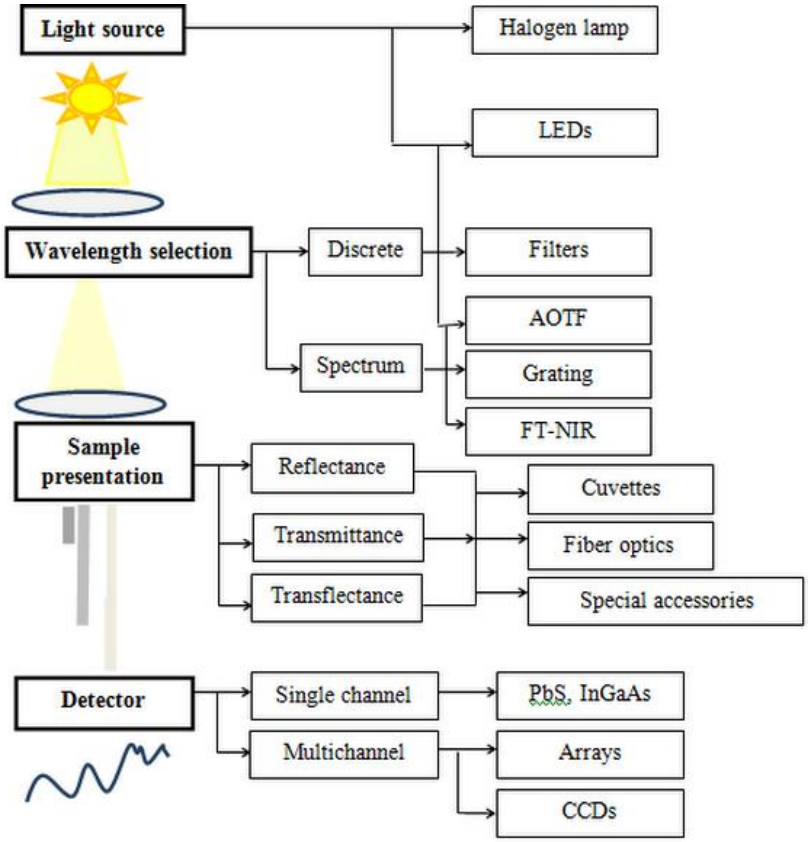

Figure 1.9: Summary of NIR instrumentation [12].

1.5.3. NIR analysis

NIR measurements are implied without dilution with short optical path lengths. UV/VIS or mid-IR spectroscopy is used as in traditional spectroscopic analysis. Either transmittance log(1/T) or reflectance (log(1/R) mode, NIR spectra can be collected.

The identification of unique spectral features related to individual chemical components is often difficult. With the purpose of improving identification, mathematical pretreatment is used in NIR technology. The second derivative of absorbance data is calculated and absorbance maxima are converted to minima with positive side-lobes. As a result, the apperent spectral bandwith is reduced allowing the resolution of overloaping peaks and eliminate baseline difference between spectra [11].

The qualitative analysis by NIR spectroskopy is based on library matching. This matchs the unknown sample with known sample, which is analysed and identified before [11]. There are two main developing approaches to classification and identification: supervised and unsupervised. Each spectrum is used for training the identification/classification algorithm in the supervised method. The algorithm of unsupervised method must identify how the number of groups within the samples can be distributed. It is employed for classification of trainin set samples and providing the model for further classifications [14].

The quantitative application of NIR pectroscopy gives not sensitive results. Consequently, most oft he quantitative applications are used for determining major components in the sample. Except some spesific applications, the dedection limit is about 0,1 % (m/m). The basis of in development, evaluation, use and maintenance of quantitative model based on NIR spectroscopy is shown in Figure 1.10.

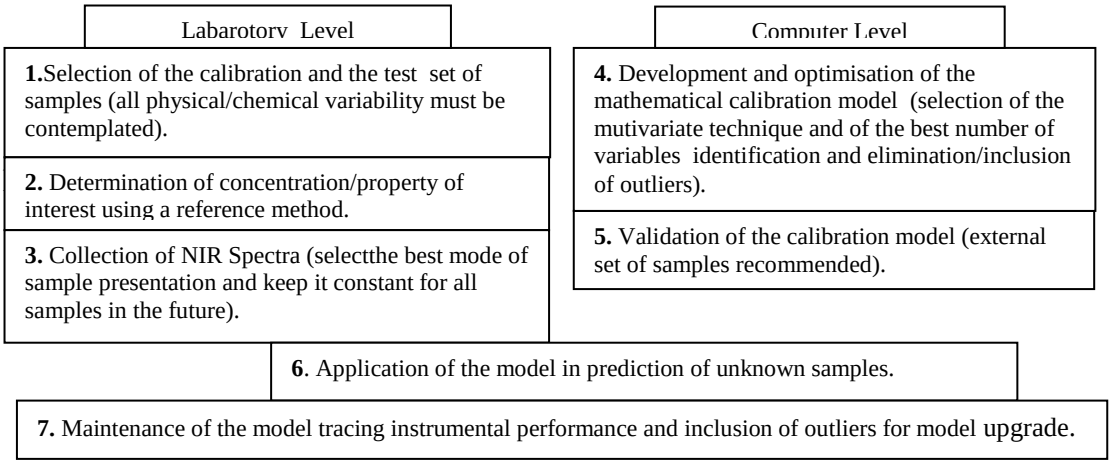

Figure 1.10: The basis of quantitative anlyse application of NIR spectroscopy [14]

In order to develop calibration models, some mathematical pre-treatment methods are used in this technology. The summary of this methods with principles are given in Table 1.6.

Table 1.6: Pre-treatment methods with working principles [13].

Pre-tretament	Basic principles
Subtraction of constant offsets	The spectra are linearly moved in order that the minimum occuring y-value will be 0.
Baseline nırmalization	In each selected frequency range a straight line is fitted to the spectrum. This line is then subtracted from each spectrum.
Standart Normal Variate (SNV)	Calculates the average y-value of the spectrum. This value is subtracted from the spectrum. The sum of the squares of all y-values is calculated and the spectrum is dvided by the square root of this sum.
Min- max normalization	The spectra are shifted linearly, in order to minimum occuring y value is set to zero. Then the spectra in the y direction can be expanded so that the maximum occurring y value is 2 absorbance units.
Multiplicative Scatter Correlation (MSC)	Each spectrum is linearly transformed so that the difference between the transformed spectrum and the average spectrum is as low as possible. This method is often applied for measurements in diffuse reflectance.
First derivative	The first derivative of the spectrum is calculated. This method is used beter distinguish peaks of overlapping bands and to filter spectral noise.
Second derivative	The second derivative of the spectrum is calculated. This method is similar to the first derivative.

After completing establishment of calibration model, applicability of model is analysed with RPD (Ratio of Performance to Derivation) and R^2 (Correlation Coefficient). Calculation of RPD is explained in Equation 1.3:

$$RPD = \frac{SD}{SEP} \tag{1.3}$$

where SD is standard deviation, SEP is standard error of prediction that shows the precision of obtained model and is calculated as following equation:

$$SEP = \sqrt{\frac{\sum^{N}{}_{i=1}\left(y^{m}{}_{i} - y^{p}{}_{i} - bias\right)^{2}}{N}} \tag{1.4}$$

where N is number of samples, y_i^m is measured property of sample, y_i^p is predicted property of sample, bias is calculated as following equation:

$$Bias = \frac{1}{N}\sum\nolimits_{I=1}^{N}\left(y_i^m - y_i^p\right) \tag{1.5}$$

All these calculations are done by NIR software and depend on RPD results, application suggestions are given in Table 1.7.

Table 1.7: Applicability of the prediction model based on RPD values [12].

RPD	Characterization	Application
≤ 2.3	Very poor	Not recommended
2.4…3.0	Poor	Very rough property estimation
3.1…4.9	Fair	Screening property estimation
5.0…6.4	Good	Quality control
6.5…8.0	Very good	Process control
>8.1	Excellent	Any application

As explained before, in addition to RPD, correlation coefficient (R^2) is used for evaluation of calibration model as in Table 1.8.

The other statistical parameters, which are used for evaluate calibration models: Root Mean Square Error of Cross Validation (RMSECV) and Root Mean Square Error of Prediction (RMSEP).

$$RMSECV = \sqrt{\left(\frac{1}{M} \times \sum\nolimits_{i=1}^{M}\left(Y_i^m - Y_i^r\right)^2\right)} \tag{1.6}$$

$$RMSEP = \sqrt{\left(\frac{1}{N} \times \sum\nolimits_{i=1}^{N}\left(Y_i^m - Y_i^r\right)^2\right)} \tag{1.7}$$

where M is number of samples in validation set, N number of samples in test set, Y_i^m is measured property of sample, Y_i^r is predicted property of sample.

Table 1.8: Applicability of the prediction model based on R^2 [12].

R^2, %	Characterization
≤ 25	Not recommended for NIR application
26…49	Poor correlation, further research is possible
50…64	Poor correlation, rough screening is possible
65…81	Fair correlation, screening and approximate calibration is possible
82…90	Good correlation, can be used with caution for most application, including research
91…97	Very good correlation, can be used for most application, including quality assurance
≥ 98	Excellent correlation, can be used for any application

2. REITBROOK PILOT SCALE BIOGAS PLANT

2.1. General Functions

In Mini fermenter the operations of a biogas plant on a small scale can be simulated. This serves to explore different substrates on their technical properties and to interpret these data by a large biogas plant on predetermined substrates.

In a biogas plant, a combustible biogas is produced with a high proportion of methane through the fermentation of organic substances under anaerobic conditions. The filling of the fermenter should ideally be carried out daily and is carried out according to their choice of components by hand or automatically [15].

For the fermentation, a hermetically closed container, which is called “fermenter”, is used. The fermented substrate is fed at regular intervals into the fermenter, so that biological processes can run evenly. The fermenter is a fermenter heating maintained at temperature and mixed by means of an agitator.

There are several parameters that affect the living conditions of the bacteria. The most important are the temperature, the pH and nutrient proportion. Biogas plants in psychrophilic range (25 – 35°C) in the mesophilic range (35 – 45°C) or be driven in the thermophilic range (45 – 50°C). From experiences, it is known that the systems run most stable in mesophilic conditions. The pH is generally between 7-8. In alike conditions, fluctation of pH give an impression of the state of biology or the biological degradation processes in the reactor [15].

In the following step, a structure of the mini fermenter will be described in details. The general appearance of Reitbrook Pilot Scale Biogas Plant is shown in Figure 2.1.

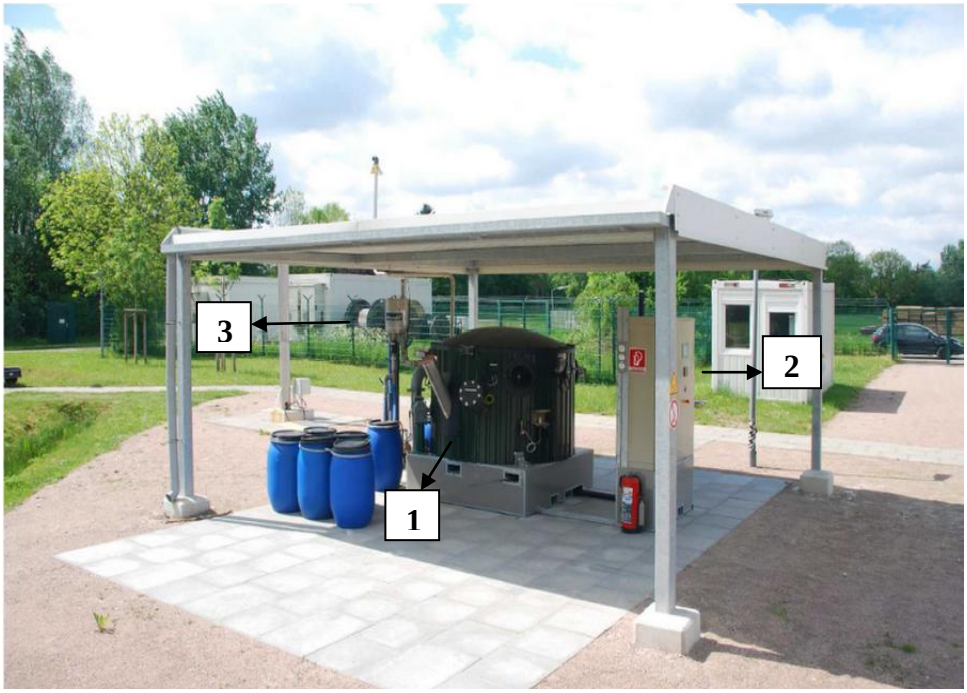

Figure 2.1: Reitbrook Pilot Scale Fermenter General Appearance; 1) Fermenter; 2)Regulation cabinet; 3) Automatic Substrate Feeding.

2.2. Structure of Fermenter

The fermenter consists of reactor, gas storage including sealing, solid entrance for manual feeding, overpressure protection and pressure safeguard, overflow fermenter contents and sampling tap for substrate, gas pipeline, gas meter, solenoid valve and manual sample tap, mixing, sight windows including light, torch and supplying pumpable substrates, which are described in more detail in the following sections [15].

2.2.1. Reactor

The reactor of the mini digester has a gross volume about 2.1 m^3. It extends from the bottom of the fermenter to the roof. For the biological process only uses the space up to the windows, that is the reactor is filled only to just below the windows. This volume is approximately 1.5 m^3. The remaining volume is available as a gas storage. The windows serve the visual control of the fermentation process (base formation, foaming, floating layers). In addition, the fermenter space can be illuminated with an explosion-proof air. The windows can be cleaned with a fixed wiper [15].

2.2.2. Gas storage including seeling

On the roof of the reactor, a membrane is installed and this area serves as gas storage. The membrane is fastened on the outside with tube which is filled with compressed air and sealed. The sealed hose is supplied via a compressor with compressed air. The pressure in that hose should be kept constant at 1,8 mbar. In support of the membrane, if it is not filled with gas, is a gas-permeable timber ceiling, placed in between the membrane and reactor. On the wooden ceiling foam panels are attached for the purpose of insulation [15].

2.2.3. Solid entrance for manual feedings

As shown in Figure below (Figure 2.2), this part is integrated in the fermenter wall. This part consists of stainless steel tube with an appropriate cover and filling tamper. The manual solids supply flows in the fermenter below the liquid level to prevent the escape of biogas into the atmosphere. The enterence is located above the liquid level.

Especially in plants without automatic feeding system, manual solids supply is used for daily feeding. Due to some eligibility of solids, usage of automotic feeding system restricted. When automatic feeding system is used, solids should be weighted before feeding. If multiple components are fed, it is recommended to mix it after weighing each other [15].

Figure 2.2: Solid entrance for manual feedings.

2.2.4. Overpressure protection and pressure safeguard

To protect the membrane, a pressure control and vacuum fuse are attached to the fermenter in order to prevent gas escape comes from product biogas produced without discharging via the gas valve. The overpressure protection is set to a pressure of 5 mbar, which corresponds to a fill height of 5 cm. This level corresponds to the maximum achievable level due to the preset angle. The pressure screen is fasten to fermenter as seen in Figure 2.2 [15].

Figure 2.3: Pressure screen of fermenter.

2.2.5. Overflow fermenter contents and sampling tap for substrate

The gravity overflow of substrat discharge occurs during operation of the Mini fermenter. Attached is the gravity overflow at the bottom of the reactor and a riser mounted. The length of the riser pipe determines the maximum level in the reactor. The tubing should be installed just below the windows. It is important to control the gravity overflow regularly and eliminate blockage with the appropriate tools [15].

To take sample, there is a sampling tap on fermenter. To obtain meaningful samples, is needed to sample valve is rinsing before taking the sample [15].

2.2.6. Gas pipeline, gas meter, solenoid valve and manual sample tap

The biogas is produced and transmitted through the gas pipe, and is released in the atmosphere or to the flare. It must be ensured that this does not take place in an enclosed space. The constant supply of fresh air must be guaranteed. The gas pipe is sealed off with a solenoid valve. The amount of discharged gas is measured by a flow meter and the value is saved and documented [15].

2.2.7. Mixing

Used substrates in biogas plants contain very different densities. To keep the fermenter contents as homogeneous as possible is used mixing technologies. In case of the pilot fermenter a correspondingly smaller version of the known from large installations, pedal mixing system is installed. The pedal mixing system is shown in Figure 2.4. The mixer is powered by an electric motor, which is mounted outside the fermenter. Via motors, rotary motion is transmitted to the shaft of the pedal mixer. Activation of the engine is via selections (manuel or automatic operation) in the control cabinet [15].

Figure 2.4: Pedal mixing system in fermenter.

2.2.8. Torch

The torch is the gas incinerating part of mini fermenter. It is attached by tubing to the gas line behind the gas meter. The biogas is after passed through the gas meter, enter the torch and burned. The torch is turned on automatically, when the gas pressure rises in the fermenter at 3.5 mbar. It closes when pressure falls below 2.0 mbar [15].

2.2.9. Supplying pumpable substrates

For application of liquid substrates such as slurry has the pilot fermenter via a liquid feed. The submersible pump is submerged in a filled with manure or similar substrate barrel. The submersible pump is connected by hose to the metering station. The metering station is a round stainless steel container with three opening stages. The pump runs and promotes substrate by one of the two corresponding chambers. If the set through the plates level achieved, the substrate flows over back in the second chamber and from there into the receiver. After the pumping set time, the desired level should be reached. The solenoid valve opens as soon as the pumping time has

ended and it closes if the light sensor determines a rest level in the dosing of approximately 5 cm [15].

3. OPERATION INFORMATION OF BIOGAS PLANT

3.1. Substrate

The pilot biogas plant was feeded daily with pellets. The feeding is started with 1 kg pellets. In order to increase dry solid content of digestate, the amount is increased to 4.5 kg step by step. The feeding amount changes are shown in Table 3.1.

Table 3.1: Feeding amount changes during operation of biogas plant.

Period (Operation day)	**1-13**	**14-90**	**91-102**	**103-107**	**107-120**
Amount (kg)	2	3	4	4.5	0
OLR (kg/m^3)	1.33	2	2.66	3	0

GB_{21} test was implied to compare biogas production capacity of pellets both in laboratory scale and in pilot scale. Before the operation perriod, dry solid content and organic solid content of pellets are tested in laboratory. The used pellets are shown in Figure 3.1.

Figure 3.1: The substrate of biogas plant: pellets.

With the aim of comparing yield of incineration and digestion technology with pellet usage, calorific bomb test was implied. The characterization of pellets by main components is shown at Table 3.2.

Table 3.2: The characterization of pellets by main components [16].

Analytical components	Percentage(%)
Crude protein	10.5
Crude oil/Fat	4
Crude fiber	2.7
Crude ash	2
Calcium	0.07
Phosphor	0.3
Sodium	0.02
Lysin	0.38
Methionin additional stage	0.2

3.2. Control Strategy

In order to supply safety and continuous biogas plant operation, it is necessary to have a sufficient control strategy. The control strategy consists of many parameters, which are mentioned in Table 3.3. With the early detection of damage and process faults, it is possible to reduce their impacts on fermentation process.

In order to check operation parameters, 5 liter digestate sample was taken once a week. pH, DM and oDM of sample were directly measured, than rest of the sample was stored for the furter laboratory and NIR spectroscopy analysis.

3.2.1. On-line methods

Large number of biogas plants have on-line controlling system. Although Germany has most improved biogas technologies, the usage of on-line controlling system is not widely used. It should be taken into consideration to improve application of on-line controlling methods [9].

Biogas production, gas composition, pH of liquid phase, alkalinity and total VFA (with using online titration) and dissolved H_2 measurements are improved as online monitıring method [18]. Hamburg (Reitbrook) Biogas Plant has an on-line controlling system. With the aim of using all on-line measurements later, they are saved directly in a memory card. The parameters which are measured online in plant are shown in Table 3.4.

Table 3.3: The control strategy of biogas plant [17].

Control frequency	Activity
Daily	On cabinet check whether fault lamps light up
	Condensate drain , discharge condensate
	Check the glycol level of the heating system
	Fermentation temperature monitor
	Ensure in all inlets and outlets , that the procedural prescribed slurry / substrate flow is maintained
	Detection of daily activity in the operation protocol
Weekly	Check fluid levels in the substrate bearing , fermenter and repository
	Control of the network connections
	Levels of overpressure protection
	Mixing propeller function check
	Visual inspection of motors and cables
	Check the function of gasmagenet-valve
Monthly	Check all slide valves , so they do not become stuck
Half-yearly	Check Electrical installations
Yearly	Control of the gas-bearing system components for damage , tightness and corrosion
	Forestry safety of sealing liquids in the overpressure protection check

Table 3.4: Online controlling parameters in biogas plant.

Controlling Parameter	Frequency of measurement	Unit
Gas Pressure	Once in hour	mbar
Power Consumption	Once in hour	kwh
Temperature	Once in hour	Celsius
Amount of Gas Production	Daily	m^3
Composition of Biogas	2 times in a week	Percentage, ppm

3.2.2. Off-line Methods

On-line controlling strategy can not be used to monitor all operation parameters. There are some researches about online controlling of VFA and oDM/DM. Because of cost, complexity or sensitivity to changes, these technologies can not be used in biogas plants easily.

In Hamburg (Reitbrook) Biogas Plant, all laboratory analysis were implied as off-line controlling method. As explained before, dry matter (DM), organic dry matter (oDM), pH, total nitrogen (TN), Ammonium nitrogen (NH_4-N), FOS/TAC, Volatile Fatty Acids (VFA) and hydrocarbonate (HCO_3^-) were tested weekly at the laboratory.

3.2.3. At-line Methods

The implied at-line controlling method at biogas plant is NIR spectroscopy. NIR Technology was used to evaluate a research; usability of this technology as the online controlling method. In order to check an accuracy of NIR analyse results, the results were compared with laboratory analysis.

4. MATERIAL AND METHOD

As mentioned before, 5 liter sample was taken every week to analyse operation parameters. The summary of implied analysis and used methods are given in Table 4.1.

Table 4.1: The summary of implied analysis and used methods.

Analysis	Standart	Title
Total solids (TS)/ Dry matter(DM)	DIN 38 414 - S 2	Determination of dry matter content
Volatile solids (VS) / Organic dry matter (oDM)	DIN 38 409-H1-3	Determination of organic dry matter content
pH value		Determination of pH value
Total nitrogen (TN)	DIN 38 409 - H 28	Determination of total nitrogen
Ammonium nitrogen (NH_4-N)	DIN 38 409 H 28	Determination of ammonim nitrogen
FOS/TAC	Nordman Method	Determination of FOS/TAC Value
Volatile Fatty Acids (VFA)	DIN 38409 - H21	Determination of volatile fatty acids
Hydrocarbonate (HCO_3^-)	DIN 38409-H7-1-2	Determination of hydrocarbonate concentration
Calorific Value	DIN EN 51900	Determination of Calorific Value for Substrate
Gas chromotogrophy (HP 6890)	-	Determination of Biogas Composition
Biogas5000 GasAnalyzer	-	Determination of Biogas Composition

4.1. Determination of Dry Matter and Organic Dry Matter Content

The total solid content is the mass ratio of dry matter to fresh mass. Determination of dry matter is carried out with three parallels for each samples. The samples are

weighted before drying. After that, the samples are dried at 105°C during 24 hours. Following the drying, samples are waited in desicator to reach room temperature [19]. Samples are weighted again and total solids contents are calculated with Equation 2.1.

$$DM = \frac{m_3 - m_1}{m_2 - m_1} \times 100\% \quad (4.1)$$

where m_1 is a mass of empty crucible (g), m_2 is mass of crucible with sample (g), m_3 is mass of crucible with sample after drying (g).

The determination of organic dry residue takes place with three parallel samples. For this purpose, each 1g of the dried sample was weighed in a porcelain crucible and then they burned in a muffle furnace at 550°C for 5 hours to constant weight. As an Equation 2.2, volatile solid content is calculated [20].

$$oDM = \frac{m_3 - m_4}{m_3 - m_1} \times 100\% \quad (4.2)$$

where m_4 is mass of crucible with sample after the ignition (g).

4.2. Determination of pH Value

To determine the pH value of digestate samples, the definition of potential difference of the media to the reference electrodeis used.

4.3. Determination of Total Nitrogen

For determining of total nitrogen (TN) the proportion of oxidized nitrogen to ammonia or amines reduced, organically bound nitrogen is converted to ammonium salts. Ammonia is expelled and determined volumetrically from the reaction mixture [21].

4.4. Determination of Ammonium Nitrogen

To determine the ammonium-nitrogen (NH_4-N), ammonia is distilled in weakly basic solution and determined in borates solution volumetrically [21].

4.5. Determination of FOS/TAC Value

In the fermentation process, strong accumulation of organic acids can cause to pH decreases. FOS/TAC value describes the ratio of volatile fatty acids (German: *flüchtige organische Säuren, FOS)* to the total inorganic carbonate (German: *totales anorganisches Carbonat, TAC*). With measuring this value, ratio of acid concentration and buffering potential in the fermentation substrate can be decided. In the experimental part, biocarbonate solution is titrated with sulphuric acid. If organic acids are present, pH drop is schifted from 5 to 3. The sulphuric acid consumption to reach pH 5.0 originated from carbonate and biocarbonate concentration. The sulphuric acid consumption between pH 5.0 and 4.4 caused by organic acids. The sulphuric acid consumption values and titration volume (20 mL) are used in FOS/TAC calculation formulas. The FOS/TAC calculation is explained in Equation 4.3, Equation 4.4 and Equation 4.5.

$$TAC(mg/L) = \frac{20mL}{V_{sample}} \times V_{TAC} \times 250 \tag{4.3}$$

where V_{sample} is sample volum (mL), V_{TAC} is volume of sulphuric acid standart solution consumed during the TAC titration (mL) [22].

$$FOS(mg/L) = \left(\frac{20mL}{V_{sample}} \times V_{FOS} \times 1,66 - 0,15 \right) \times 250 \tag{4.4}$$

$$FOS/TAC = \frac{FOS(mg/L)}{TAC(mg/L)} \tag{4.5}$$

4.6. Determination of Volatile Fatty Acids

50 mL samples in three parallels are steam distilled with concentrated phosphoric acid. Potentiometric titration method is used for determining volatile fatty acids (VFA) content. NaOH is used as a titrant and phenolphthalein is used as a indicator.

4.7. Determination of Hydrocarbonate Concentration

This experiment based on acidification of sample by 0.1 M HCl solution with methyl orange indicator. With the help of methyl orange solution, pH 4.3 point is detected.

At this point only carbon dioxide (CO_2) is present in the sample. This procedure is implied on three parallel samples.

$$HCO_3^- + H^+ \leftrightarrow CO_2 + H_2O$$

Hydrocarbonate concentration is calculated as shown in Equation 4.6, with using HCl consumption volume during the titration.

$$Ks4.3 = \frac{C(HCl) \times V_1 \times 1000}{V_2} \quad (4.6)$$

where C(HCl) is hyrolic acid concentration (M), V_1 consumed volume to reach pH value of 4.3 (mL), V_2 sample volume (mL) [23].

4.8. Determination of Calorific Value for Substrate

Calorific value or heating value are reaction energies (during combustion under constant volume) or reaction enthalpy (in combustion under constant pressure), which are emitted by the system and therefore provided with a negative sign.

In this case, the principle is provided that the temperature of the reaction products after the combustion is equal to the temperature of participating in the reaction components prior to combustion.

According to DIN EN 51900-1, the calorific value of the sample is calculated as Equation 8 in joules per gram.

The quotient of the amount of heat that is released during complete combustion , and the mass of the sample referred to under the following assumptions :

- The combustion takes place at constant volume
- The temperature of the fuel before combustion and that of its combustion products is 25°C
- The existing water and the water formed during combustion of the hydrogen-containing compounds of the fuel are after combustion in the liquid state prior to burning the fuel
- The combustion products of carbon and sulfur are present as carbon dioxide and sulfur dioxide in the gaseous state
- Oxidation of the nitrogen has not occurred.

It is determined using the method described withure a bomb calorimeter.

$$H_{O,V} = \frac{C \times \Delta T - (Q_N + Q_S + Q_Z)}{m_p} \quad (4.7)$$

where $H_{o,v}$ the calorific value of the sample (J/g) , ΔT the temperature change (K) , Q_N the generation of heat by the formation of nitric acid (J) , Q_S the generation of heat by forming SO_2(J), Q_Z the foreign amount of heat (J) , m_p the mass of the sample (g).

C the heat capacity of the calorimeter, determined in Joule per Kelvin, according to Equation 15:

$$C = \frac{H_{O,V} \times m_B + Q_Z}{\Delta T} \quad (4.8)$$

where $H_{o,v}$ the calorific value of the reference substance (J/g), m_B the mass of the reference substance (g) , Q_Z the foreign amount of heat (J) , ΔT the determined during calibration temperature increase (K) [24] .

4.9. Determination of Biogas Formation Potential

For the determining biogas formation potential, three parallel batch tests are implied in mesophilic conditions as defined German standard procedure VDI 4630. The general set up of this test is shown in Figure 4.1. The experiment set up consist of liquid sample bottle, gas collection tube, barrier solution tank and gas sampling parts.

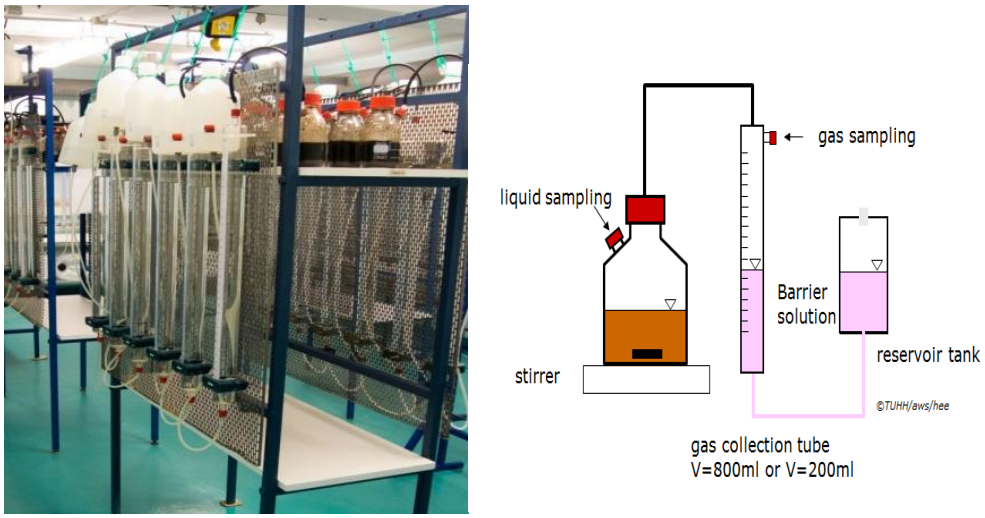

Figure 4.1: The set-up of GB_{21} test [12].

In the sample preparation part 0.5 L bottles were filled with 3 g of substrate and 200 mL of inoculum from the sewage plant. The pH values are measured before and after test to control the range 6.8 – 8.2. HCl or alkalizing solutions can be used for arranging pH value. After all these steps, filled bottles are degassed and experiment set up is established in mesophilic conditions (T= 35 ± 1°C). Until reach constant negligible gas production volume (normally it takes 21-40 days), the volumes are recorded for each samples per daily.

Biogas formation from inoculun itself is measured during the experiment without substrate addition to experiment bottle. Three parallel reference test bottles are prepared with using a mixture of 0.64 g of micro-crystalline cellulose and 200 mL of inoculation sludge and the test is implied in same conditions with samples.

The calculation of specific biogas formation potential is shown as followings (Equation 4.9):

$$V_S = \frac{\sum V_0 \times 10^4}{m \times DM \times VS} \tag{4.9}$$

where V_s is specific biogas formation potential related to VS content ($L_N \cdot kg_{VS}^{-1}$), m is subtrate mass (g), V_0 net biogas production volume from the substrate under normal conditions (calculeted in Equation 4.10) [12].

$$V_0 = V \times \frac{(P_L - P_W) \times T_0}{P_0 \times T} \tag{4.10}$$

where V is volume of generated biogas (mL), P_L is air pressure (hPa) , P_W is vapor pressure of the water (hPa), T is normal temperature (K) , P_0 is normal pressure of 1,013 hPa.

4.10. Determination of Biogas Composition

The biogas content of biogas plant was anaysed with a mobile as analyser. In order to validate results of analyser, gas chromatography was used.

4.10.1. Biogas5000 gas analyser

The biogas content is analysed in plant with using Biogas5000 gas analyser by dual-beam IR absorption. After calibration with ambient air; CH_4, CO_2, O_2 and N_2 were

measured in percentage. H_2S were dedected up 1000 ppm concentration. The biogas5000 gas analyser is shown in Figure 4.2 with gas sample bag.

Figure 4.2: Biogas5000 gas analyser.

4.10.2. Gas chromotography

The gas chromatography (type HP 6890) was used for determining biogas composition with using thermal conductivity dedector.

4.11. Near Infrared (NIR) Spectroscopy

In order to develop a model for application of faster analyses than laboratory analyses of digestate, NIR spectroscopy were used. MPA Multi Purpose FT-NIR Analyser (Bruker®, Germany) with installed OPUS software was used for NIR analyses of digestate samples. As shown in Figure below (Figure 4.3), beam path consist of interferometer, filter, NIR light source, dedector, integrating sphere and sample area.

The samples were taken from biogas plant weekly (during 120 days) and they were stored in freezer for further NIR analyses. After collection of all samples, they were analysed by NIR in three parallels. As shown in Figure below (Figure 4.4), a sample was filled in a glass flask. The flask was placed special hole on the top of NIR window, and 'Measuring – Adjustment mode' a peak position of interferogram (Figure 4.5) was saved in dialog window.

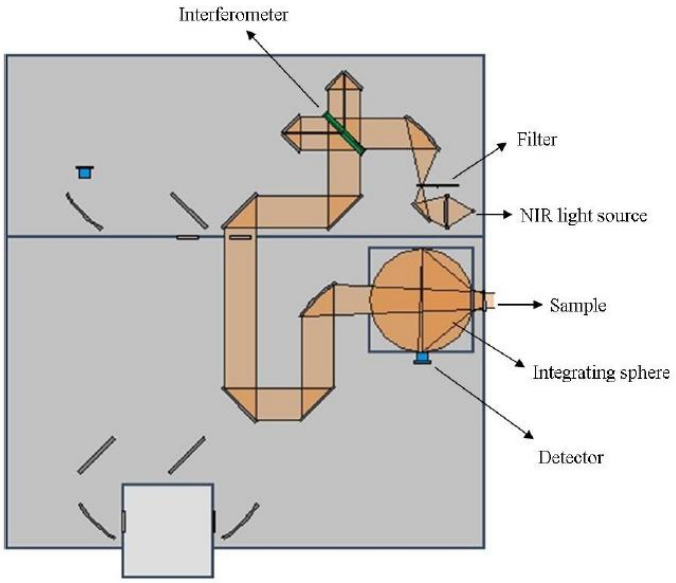

Figure 4.3: Beam path in the Bruker Optics spectrometer [13].

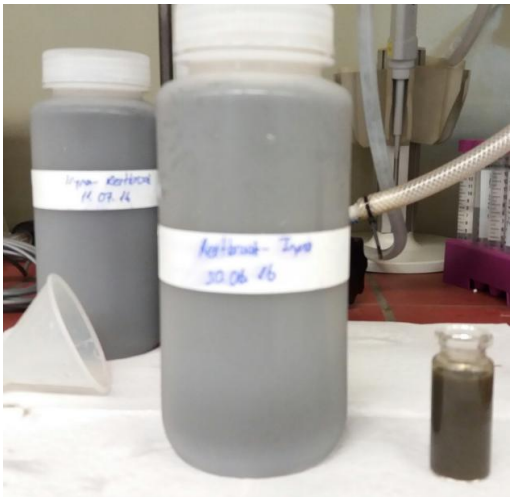

Figure 4.4: Display of sample preperation for NIR spectroscopy.

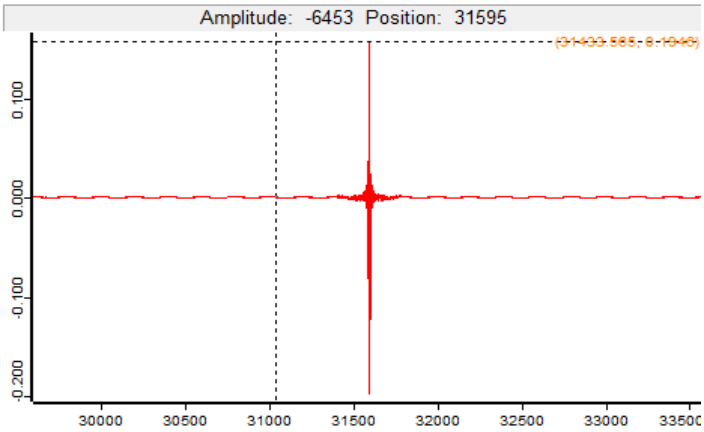

Figure 4.5: The interferogram for digestate samples.

Each samples were scanned over NIR wavelength from 12.500…3.600 cm^{-1} (800 - 2.778 nm) and resolution 8 cm^{-1}. Number of scans per spectrum was adjusted to 256. Analyses were implied in three parallels for each sample, that means; reloading used sample, mixing and refilling new sample in glass flask. The general measuring parameters can be arrayed as; resolution, measuring time of sample, measuring time of background and wavelength range. The selected parameters are given in Table 4. 2.

Table 4. 2: Selected parameters for NIR analysis.

Parameter	Value	Unit
Resolution	8	cm^{-1}
Measuring time of sample	256	scans
Measuring time of background	32	scans
Wavelength range	12.500- 3.600	cm^{-1}

After obtaining the spectras from each sample, best pretreatment methods were found with using optimisation window in OPUS software. The quality of calibrations was evaluated by R^2, RMSEC, bias and RPD results.

5. RESULTS AND DISCUSSION: EVALUATION ADOPTION STRATEGY

All analyses, which were applied to digestate from Pilot Biogas Plant, (Reitbrook) were carried out in 2 parallels: NIR spectroscopy and labartory analyses. In the following section, development of NIR technology for biogas monitoring parameters and labarotory analyses will be explained. Laboratory analyses include: DM, oDM, pH, TN, FOS/TAC, VFA, HCO_3^-, NH_4-N, calorific value of pellets, biogas potential of substrate and biogas composition of biogas plant. In addition to all these parameters, biogas production rate, temperature, pressure, energy consumption of biogas plant will be explained in following sections.

5.1. Biogas Production Rate During the Operation Time

As mentioned before in Table above (Table 3.1), the feeding amount was increased from 1 kg to 4.5 kg during operation time. Daily biogas production volume changed between 0.5 – 1.4 m^3. Depend on operation conditions and irregular feeding frequency, biogas production fluctations were observed. Organic overload was observed after 90th operation day. After that, substrate feeding was stopped for 10 days to reach normal conditions. The general view of daily biogas production and feeding amount changes within operation period aregiven in Figure 5.1.

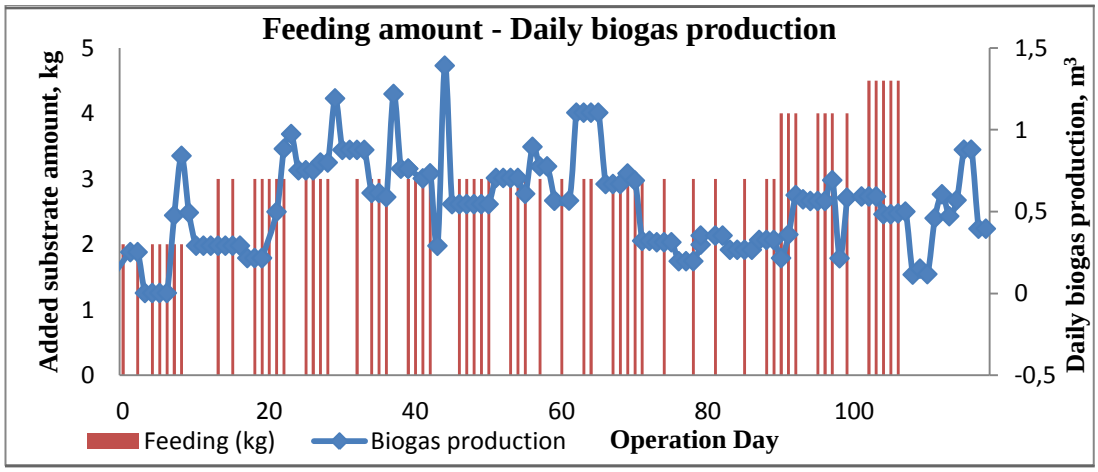

Figure 5.1: Display of Daily Biogas Production with Feeding Amount.

5.2. Development of Methane Content of Biogas

Accumulated biogas volume information were taken daily from biogas counter at biogas plant. The mean methane content was calculated seperately for different operation periods. Depend on these calculations, the daily and accumulated CH_4 prouction volume was calculated. As seen in Figure below (Figure 5.2), from daily production volumes, fluctations can be seen clearly. Until 90^{th} operation day, the CH_4 production fluctations were caused from feeding frequency changes. But after that, heating system failure came true. With the effect of this failure, CH_4 content of biogas was decreased.

As can be seen in Figure 5.2, the lack of feeding time spreaded within operation time. Between 15^{th} - 20^{th} , 30^{th} - 35^{th} and 45^{th} - 50^{th} operation days, scarcity of substrate can be seen clearly. Between 70^{th} and 90^{th} operation days, the frequency of feeding was lower than past operation days. As a result, methane percentage of biogas composition was decreased at that times.

Because of the heating system failure, temperature of biogas plant was decreased to 30°C for first failure week, in second week around 25°C and then 20°C. These temperature ranges had negativelly effect on digestion microbiology which live in mesophilic conditions. And it effected to methane production capacity of microorganisms negatively. In this period, CH_4 percentage was decreased to between 20% and 30%.

5.3. Composition of Biogas within the OperationTime

As mentioned before, CH_4 composition of biogas was nearly same until 90^{th} operation day. In that period, the CH_4 percentage fluctuated between 40% and 50%. Heating system failure was affected CH_4 composition of biogas. During this time, H_2S concentration was increased average from 400 ppm to 600 ppm. In addition to heating system failure, high concentrations of H_2S had negattiv impact on fermentation process. CH_4 percentage and H_2S concentration of biogas are given in Figure 5.3. In addition, other components (CO_2, O_2 and N_2) of biogas which are not given in Figure below, are presented in Table A.2.

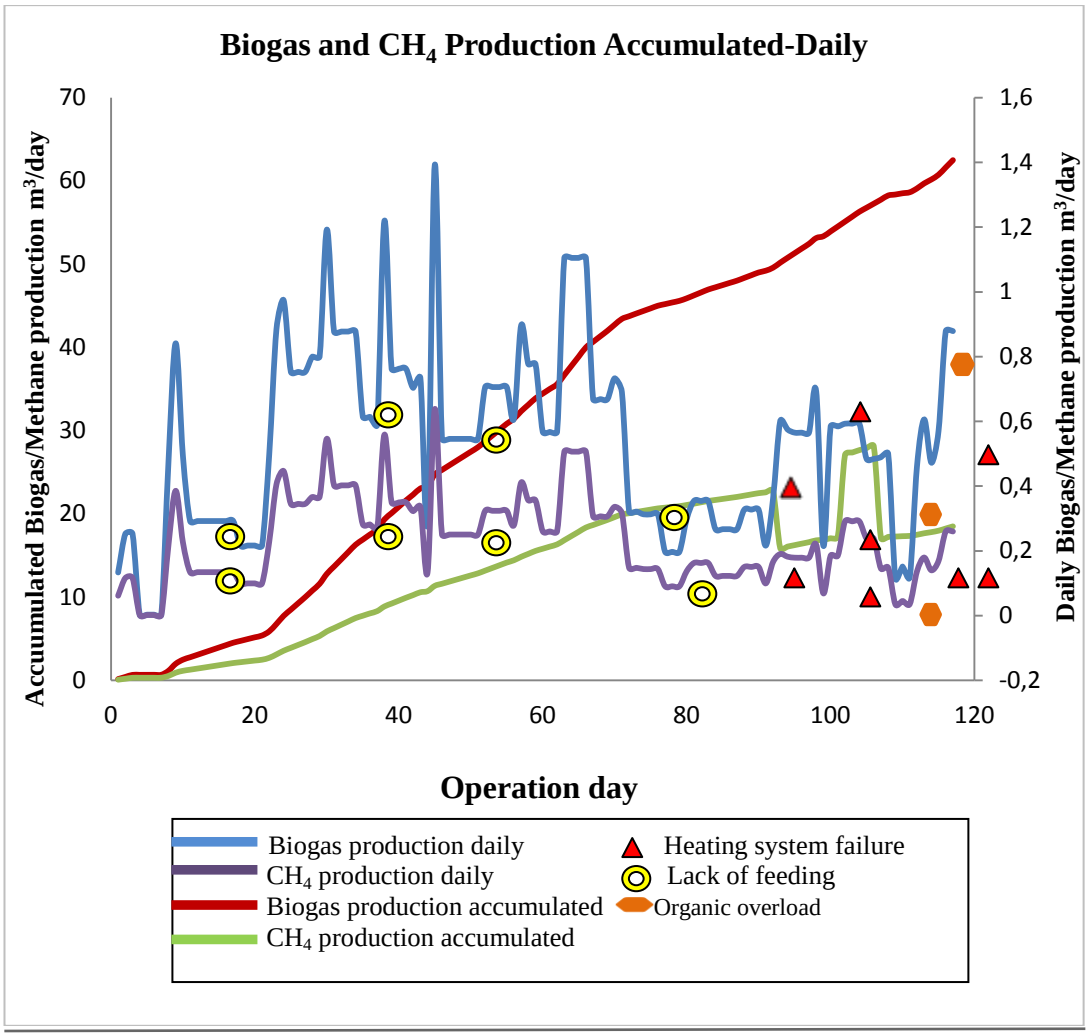

Figure 5.2: Daily and accumulated volumes of CH_4 and biogas.

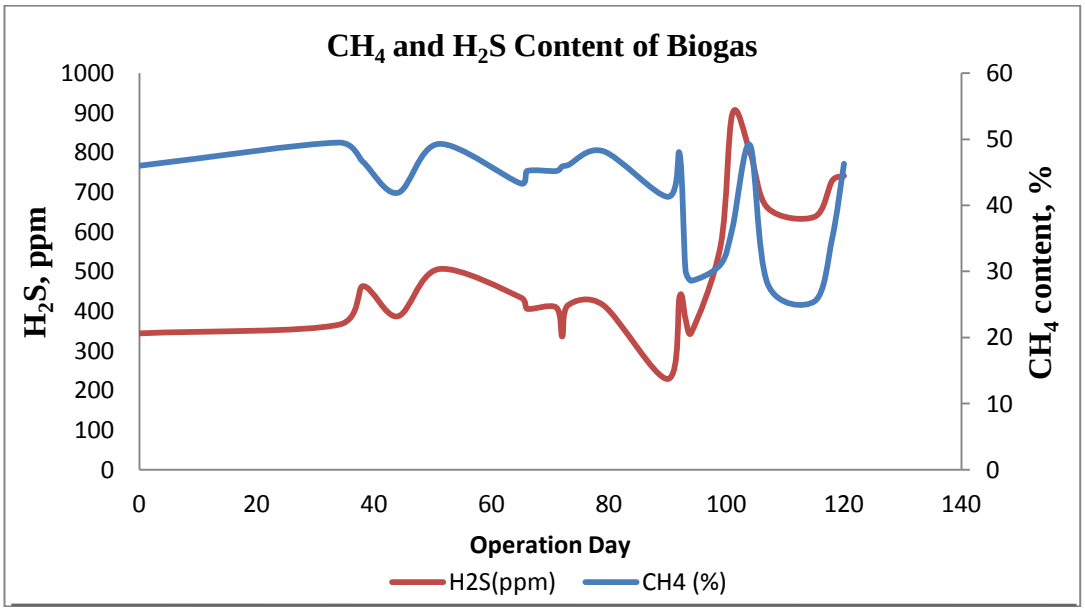

Figure 5.3: CH_4 and H_2S content of biogas.

5.4. Comparision of Energy Production and Energy Consumption

Information of biogas plant energy consumption was taken daily from biogas plant and it was saved hourly in memory card. For comparision, energy production of plant was calculated with using daily biogas production and gas composition analyses results. It is accepted that the energy production capacity of biogas is 6 kWh/m^3 [25]. Energy consumption includes both heat and the other necessary expenditures. Because of that, energy production was calculated as total of heat and electricity production. In operation time (within 120 days) 2500 kWh energy consumed by biogas plant. Despite all the operational problems, accumulated energy production reached to 500 kWh. The comparision of energy production and consumption of biogas plant is shown in Figure below (Figure 5.4) and all data are presented in Table A.1.

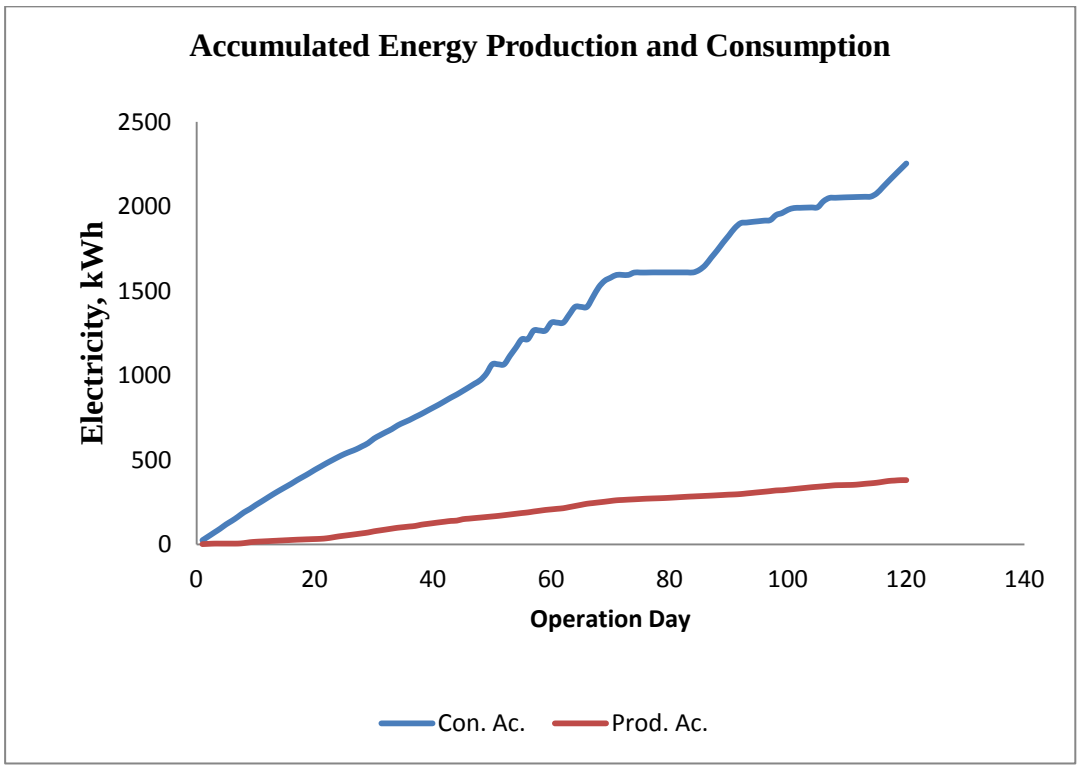

Figure 5.4: Comparision of Energy Production and Energy Consumption Amounts.

The temperature of environment was taken into consideration to compare energy consumption of operation months. Because of failure at monitoring system in May, hourly and daily temperature changes information could not be taken. Unlike other operation months, energy consumption is quite high during March. Due to low environmental temperature during day and night, heating system needed more enegy.

As can be seen in Figure below (Figure 5.5), electricity consumption changed between 20 kWh and 25 kWh.

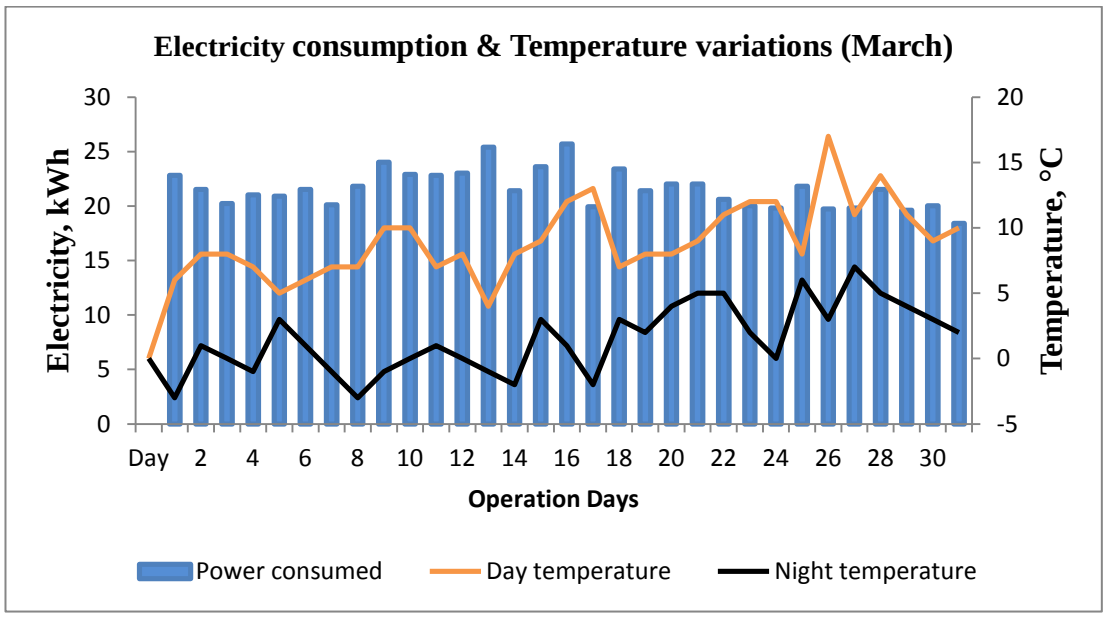

Figure 5.5: Electricity consumption & Temperature variations (March).

In April, mean energy consumption is 25 kWh. Because of monitoring system failure, end of the April energy consumption reaches 60 kWh. Day and night temperatures with energy consumtion for April are given in Figure below (Figure 5.6).

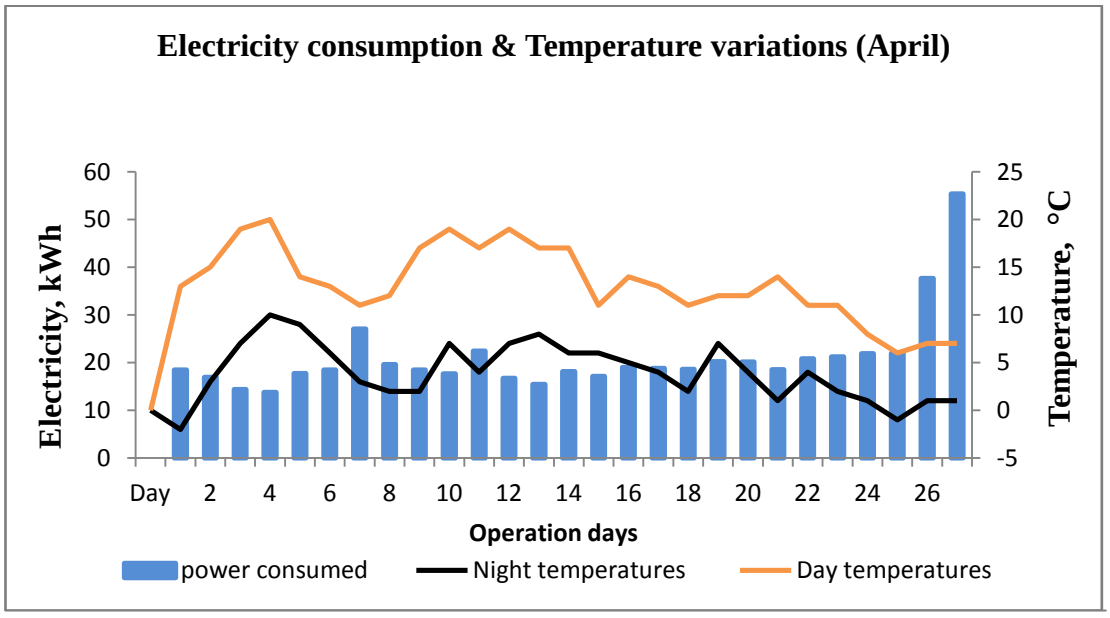

Figure 5.6: Electricity consumption & Temperature variations (April).

Due to monitoring system failure, the data of energy consumption was not reachable. A similar situation as an April, energy consumption in June has huge fluctations. The fluctations are shown in Figure below (Figure 5.7), which caused from monitoring system failure.

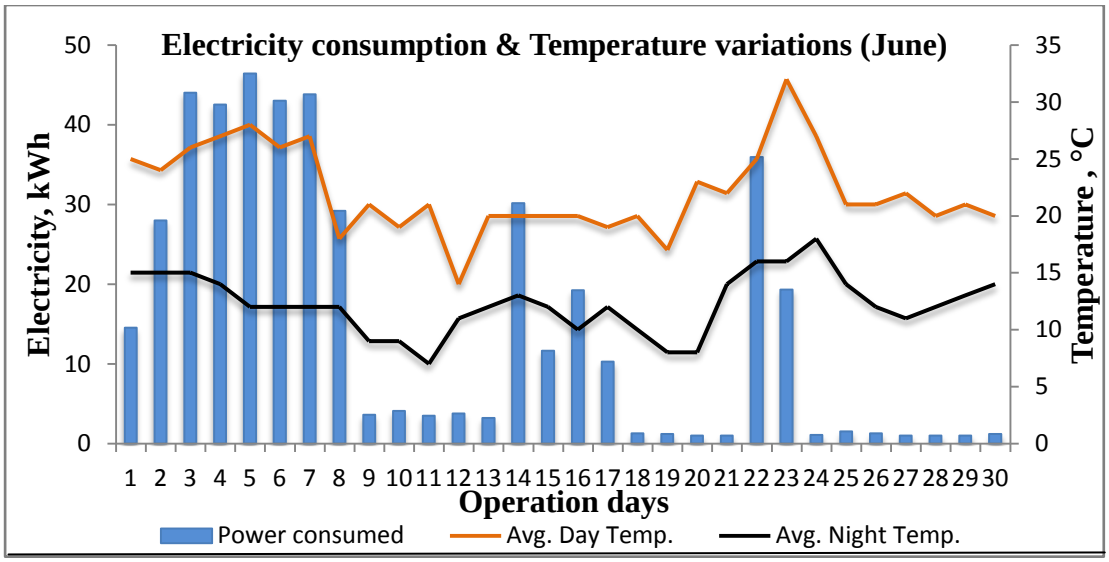

Figure 5.7: Electricity consumption & Temperature variations (June).

Similar to other months, reliable energy consumption data could not be observed in July. In Figure below (Figure 5.8) it can be clearly seen that environmental temperature is quiet high. Because of that, energy consuption should be lower than other operation months.

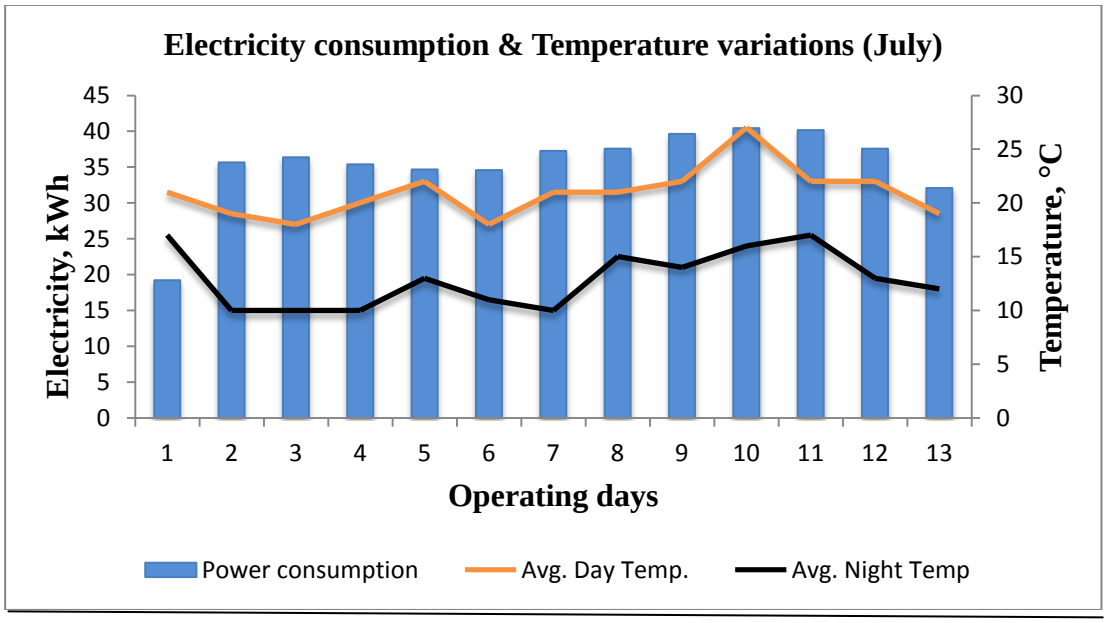

Figure 5.8: Electricity consumption & Temperature variations (July).

5.5. The Measurments of Temperature and Pressure in Biogas Plant

As explained before, every minute temperature and pressure measurements were saved in a memory card at biogas plant. Temperature was mesured around 40°C until heating system failure at 80th operation day.

During first 10 operation days, the pressure gauge was failed. Therefore, pressure was measured under 1 mbar as shown in Figure 5.9. Until 50th operation day, pressure measurements were taken in reliable way. Although pressure of fermenter should not be higher than 5 mbar, higher than 5 mbar readings were observed.

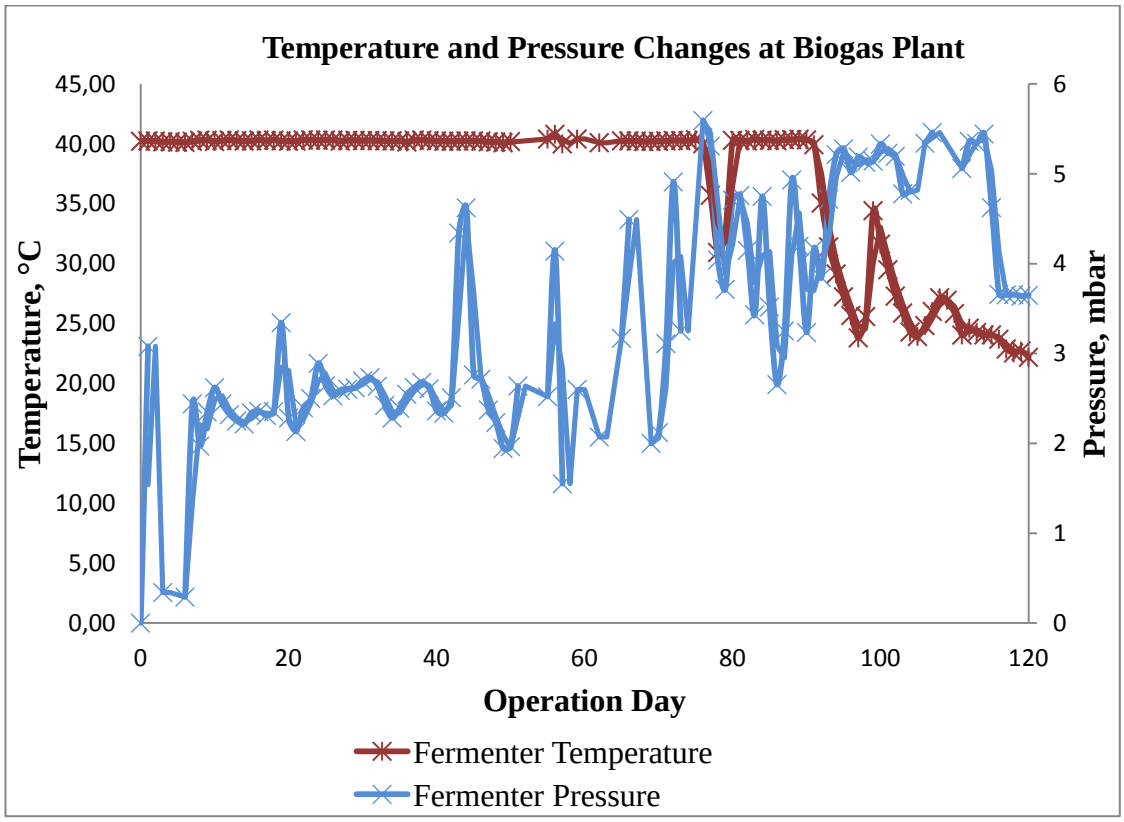

Figure 5.9: Temperature and Pressure Changes at Biogas Plant.

5.6. Results of DM and oDM Analyses

Dry matter content (DM) of digestate increased from 1.5 % to 2.8 %. As DM content, organic dry matter content (oDM) was increased from 71 % to 77 %. The changes were parallel to feeding amount changes. As shown in Figure below (Figure 5.10), there was not huge fluctations for all parameters.

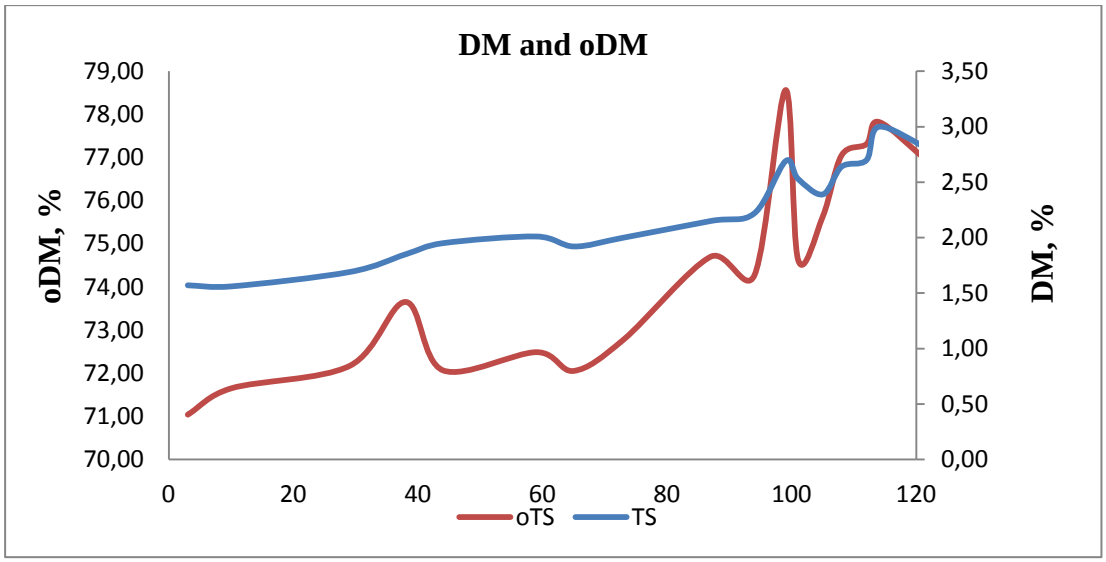

Figure 5.10: DM and oDM Results.

5.7. Results of FOS/TAC and pH Analyses

During 90 days, pH was stabil with small fluctations. Like the other parameters, pH and FOS/TAC was effected from organic overload and heating system failure. It caused to pH decreases and FOS/TAC increases. The general situation is shown in Figure below (Figure 5.11).

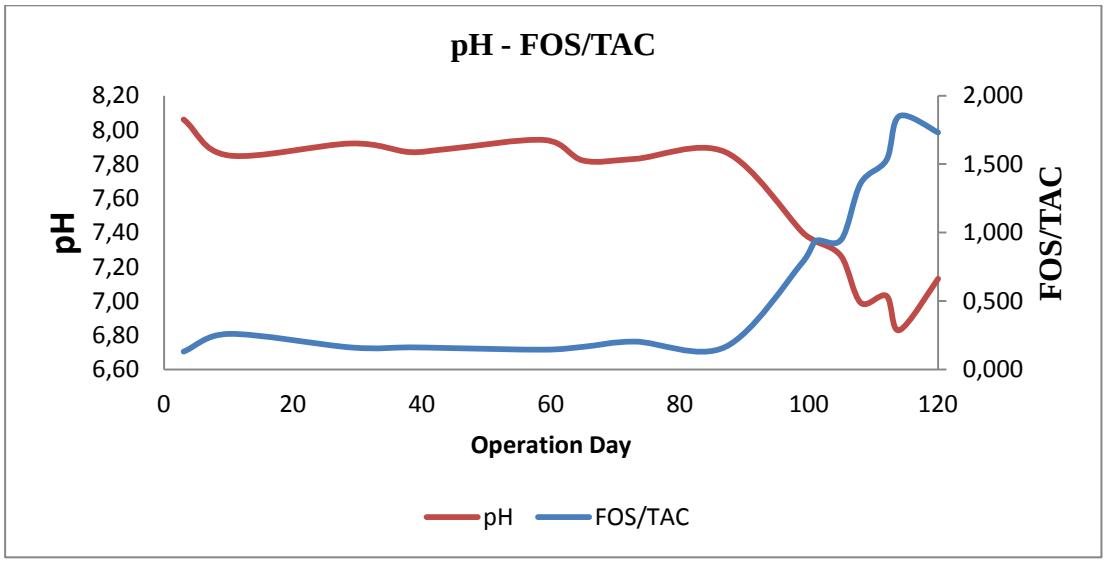

Figure 5.11: Display of pH and FOS/TAC Results.

5.8. Results of NH_4-N and TN_{CD} Analyses

The range of NH_4-N was between 3600 mg/L and 4400 mg/L. The fluctations of NH_4-N concentrations are given with TN_{CD} concentrations in Figure 5.12. TN_{CD} concentration was fluctated between 4.9 mg/L and 6.85 mg/L.

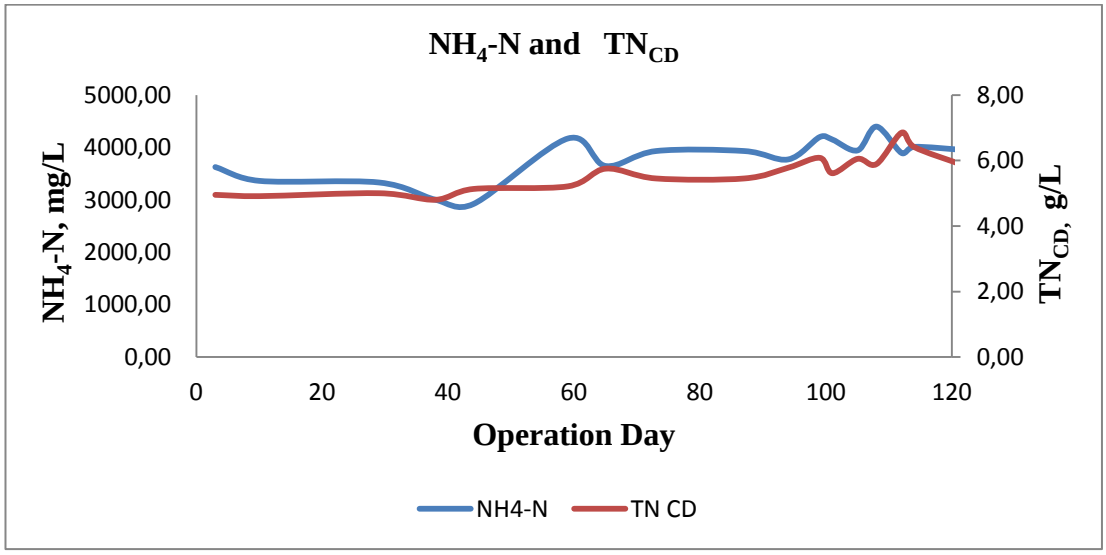

Figure 5.12: Display of TN_{CD} and NH_4-N Analysis.

5.9. Results of VFA and HCO_3^- Analyses

As seen until 90th operation day, VFA concentrations were between 70 mg/L and 500 mg/L. As has been explained in Chapter 5.1, organic overload problem was observed. For this reason VFA concentration scaled up to 13000 mg/L. The concentration changes of VFA and HCO_3^- are shown in Figure 5.13.

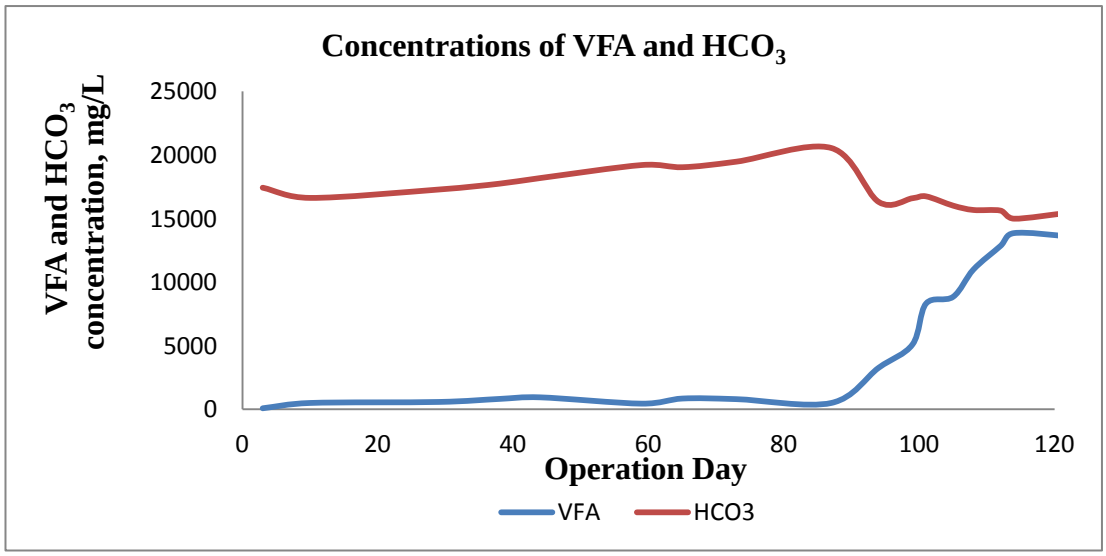

Figure 5.13: Concentrations of VFA and HCO_3^- within operation time.

5.10.Result of Calorific Value Test of the Substrate

In order to compare anaerobic digestion and incineration technology for pellets, calorific value test was applied. As a result of two parallel test, 17635 J/g obtained as main value. All results are given in Table 5.1.

Table 5.1: Results of Calorific Value Test.

Sample	Calorific Value	Mean Value
Pellets-I	17650 J/g	17635 J/g
Pellets-II	17619 J/g	

5.11. Results of Biogas Potential Test of Substrate at Laboratory Scale

In order to test biogas potential of substrate in laboratory scale, GB_{21} test was applied to pellets in three parallels. During 30 days, information of biogas production volume of substrate was saved. After biogas production volume reached to stabil amount, the test was completed. As shown in Figure below (Figure 5.14), accumulated biogas generation volume was calculated in mL/g oDM within experiment operation.

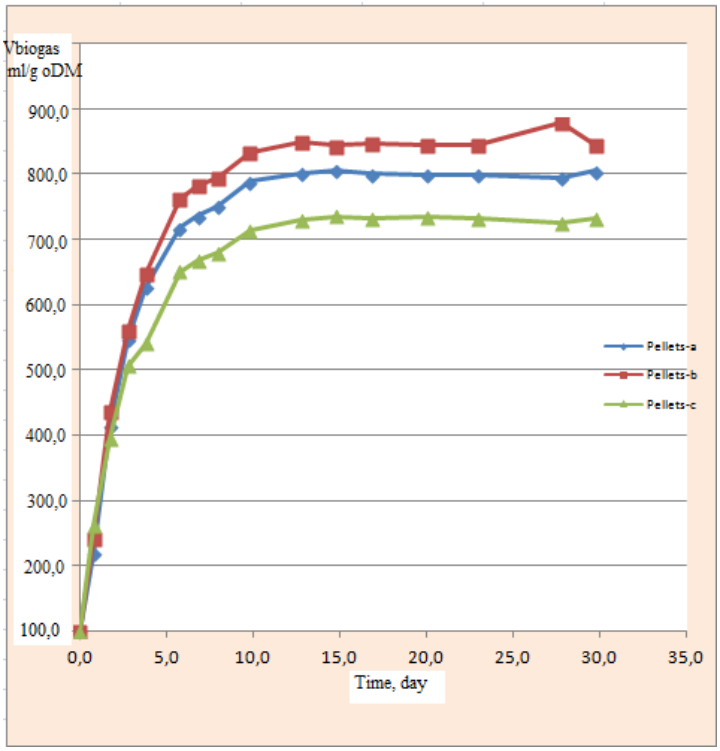

Figure 5.14: Results of Biogas Potential Test for Substrate.

Information of biogas generation volumes per wet matter, dry matter and organic dry matter were given in Table 5.2.

Table 5.2: Results of Biogas Potential Test for Substrate.

	Result	Unit
Per wet matter (FM)	582.5 ± 47.14	$ml_N.(g\ FM)^{-1}$
Per dry matter (DM)	673.8 ±55.47	$ml_N.(g\ DM)^{-1}$
Per organic dry matter (oDM)	692.4 ± 57.67	$ml_N.(g\ oDM)^{-1}$
DM content of substrate	86.45	% DM
oDM content of substrate	97.31	% oDM

5.12. Results of NIR Spectroscopy: Quantitative Analyses

The parameters; HCO_3^-, oDM, DM, NH_4-N, TN and VFA were analysed quantitatively with NIR spectroscopy. In order to decide realibility of results, they were compared with laboratory results.

Original spectra of measurements are given in Figure below (Figure 5.15). It is clear that spectras have homogeneous dissociation. However, it can be seen baseline offsets and bias. Because of that, spectral further pre-treatment is necessary to establish a calibration model.

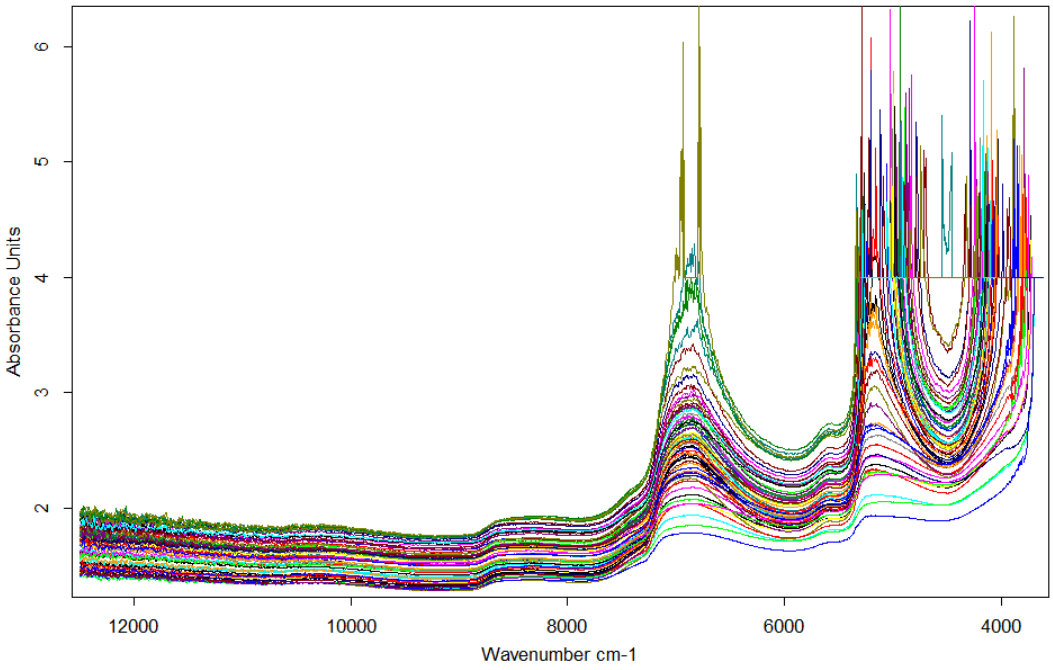

Figure 5.15: The original view of the digestate samples.

5.12.1. Calibration model establishment

The calibration model was developed with 24 random selected digestate samples from biogas plant. Each sample are scanned and optained a spectra. Depend on R^2 and RPD value of each parameter, the calibration model was established with or without pre-treatment. The best results of calibration model developing for Reitbrook Biogas Plant are given in figures below. As explained in Tables above (Table 1.7 and Table 1.8), the applicability of models was evaluated with R^2 and RPD value.

As can be seen in Figure below (Figure 5.16) the best calibration model obtained without pretreatment for dry matter (DM) content. This calibration model has correlation coefficient of 94.81 % and RPD of 4.39, which gives oppurtunity to screening property estimation for digestate samples. The report of this calibration model was given in APPENDIX C: Calibration Model Establishment with NIR Spectroscopy

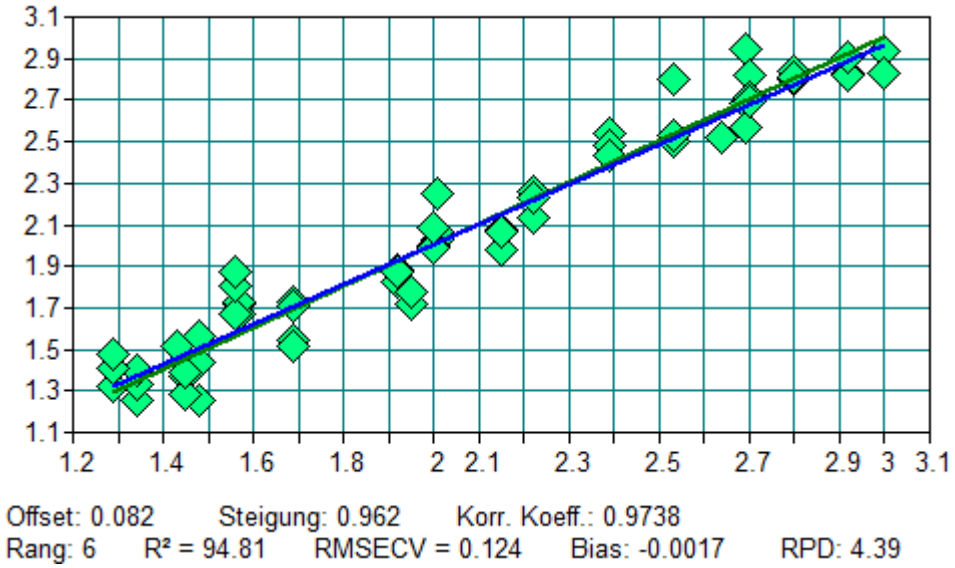

Figure 5.16: Calibration model for DM - without pretreatment.

For oDM, the best calibration model was obtained with implementation of min-max normalisation calibration method which datas were given in Table C.2. As is shown in Figure below (Figure 5.17), the model has correlation coefficient of 87.3 and RPD of 2.82. Based on this results, very roughly oDM estimations can be obtained for test samples.

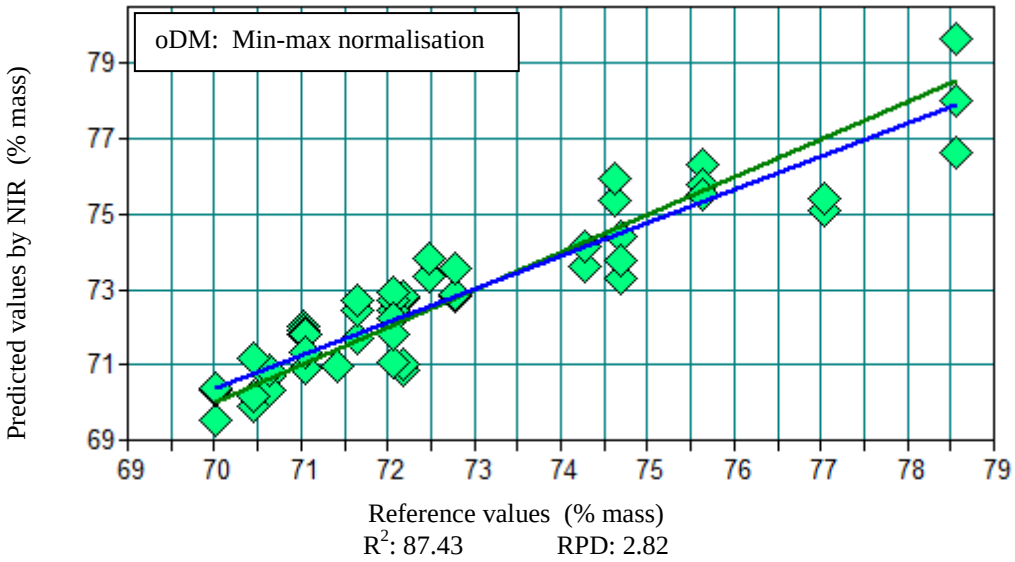

Figure 5.17: Calibration model for oDM - min-max normalisation method.

Substraction of constant offsets pretreatment method was applied to obtain best calibration model for TN analyses. As shown in Figure below (Figure 5.18), correlation coefficient of 87.74 % and RPD of 2.86 value was observed, which means it is applicable for very roughly analyses. For detailed information, all datas can be found in Table C.3.

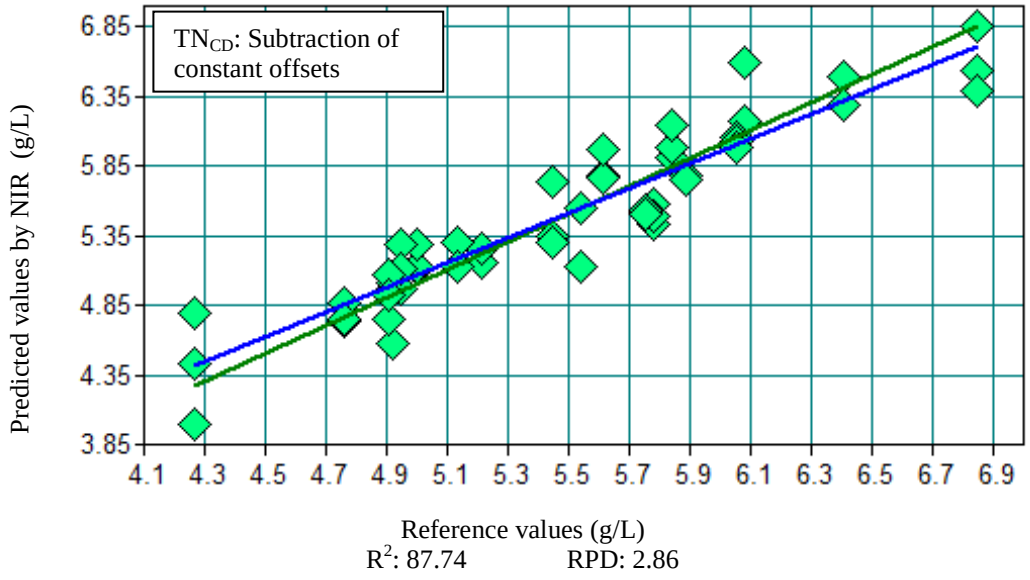

Figure 5.18: Calibration model for TNCD - Subtraction of constant offsets.

As result of oDM calibration model establishment, min-max normalisation method was used to obtain best calibration model of VFA with results in Table C.4. As can be seen in Figure 5.19, the estimated values by NIR were not acceptable as result.

Despite correlation coefficient is high (87.16 %), RPD of 2.79 was observed. As a result of these values, which are shown in Figure below (Figure 5.19), this model can be used for very roughly estimation for VFA test.

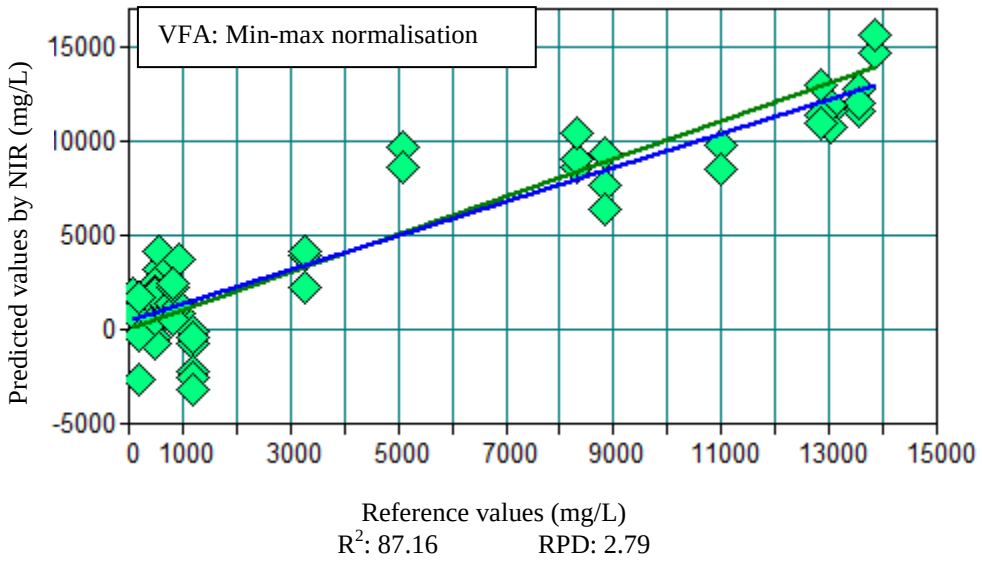

Figure 5.19: Calibration model for VFA - min-max normalisation.

Different from other applied pretreatment methods, multiplicative scatter method was used for establishing calibration model of NH_4-N. The calibration model is shown in Figure below (Figure 5.20), which has correlation coefficient of 84.26 % and RPD of 2.53. Similar to other models, this model can be used for very roughly estimations. Report of this model is given in Appendix C.

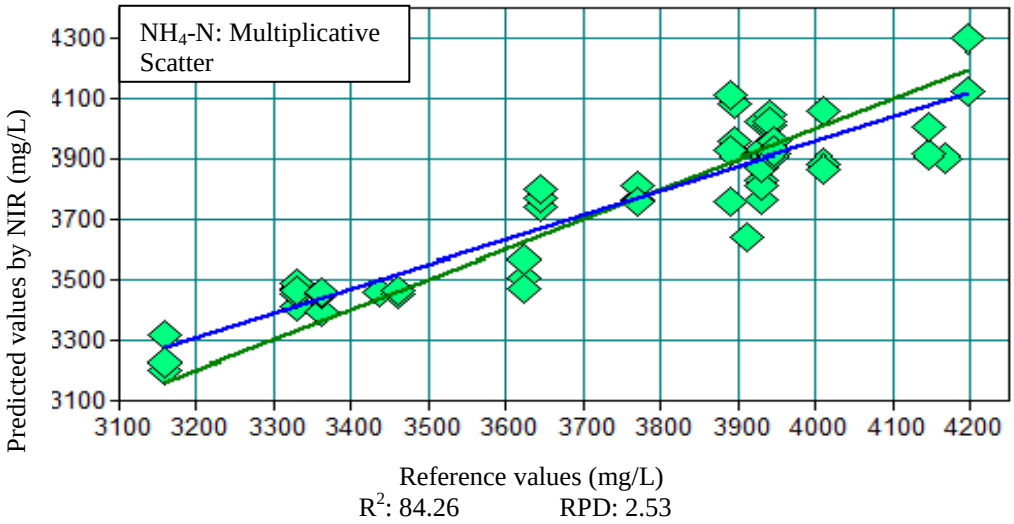

Figure 5.20: Calibration model for NH4-N - multiplicative scatter.

In order to obtain best calibration model for HCO_3^-, minmax normalisation method was used. As shown in Figure below (Figure 5.21), coefficient coefficient of 70.74 % and RPD of 1.85 was obtained as result of calibration model establishment. Because of low RPD value, this model is not recommended to use. More detailed report can be seen in Table C.5.

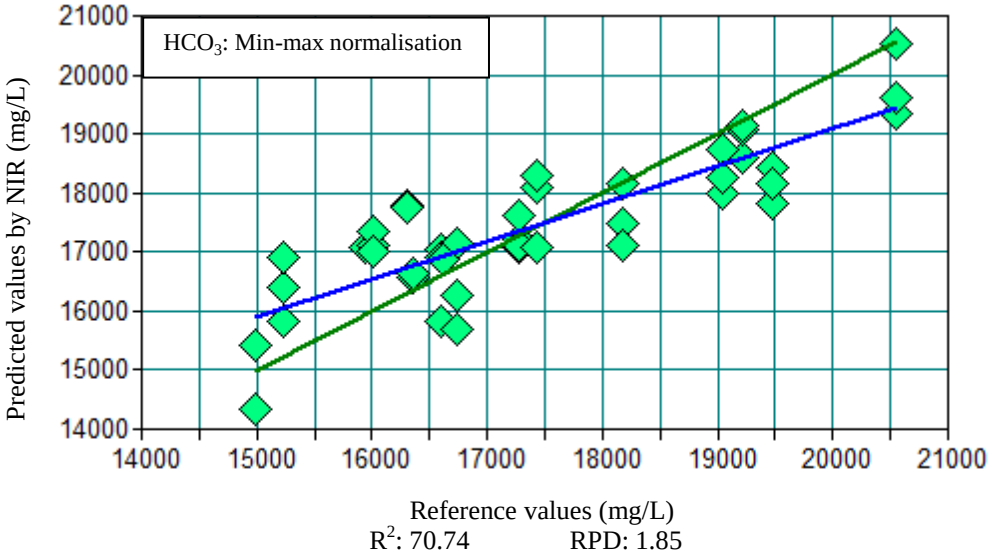

Figure 5.21: Calibration model for NH_4-N - min-max normalisation.

In Table below (Table 5.3), the summary of calibration models are given with characterisations depend on R^2 and RPD value. As a result of evaluation, application of models can be decided by using Table 1.7 and Table 1.8. The characterization of model by R^2 and RPD is rather controversial. Based on R^2 it is good correlation, whereas based on RPD it is poor. These applicability variations can be originated from improvement aim of RPD. Applicability evaluations based on value of RPD were developed for agricultural and food industry.

5.12.1.1. Test of calibration model

In order to test another samples, which had not got results of some analyses, the samples were scanned in triplicate by NIR. Same wavelenghts and same parameters were used to test samples. First of all, calibration model methods (Figure 5.22) were uploaded in dialog window for oDM and HCO_3^-.

Table 5.3: Summary of calibration models for biogas plant.

Parameter	R^2	Characterisation of R^2	RPD	Characterisation of RPD	Application
DM	94.81	Very good correlation	4.39	Fair	Screening property estimation
oDM	87.43	Good correlation	2.82	Poor	Very roughly property estimation
TN_{CD}	87.74	Good correlation	2.86	Poor	Very roughly property estimation
VFA	87.16	Good correlation	2.79	Poor	Very roughly property estimation
NH_4-N	84.26	Good correlation	2.53	Poor	Very roughly property estimation
HCO_3^-	70.74	Fair correlation	1.85	Very poor	Not recommended

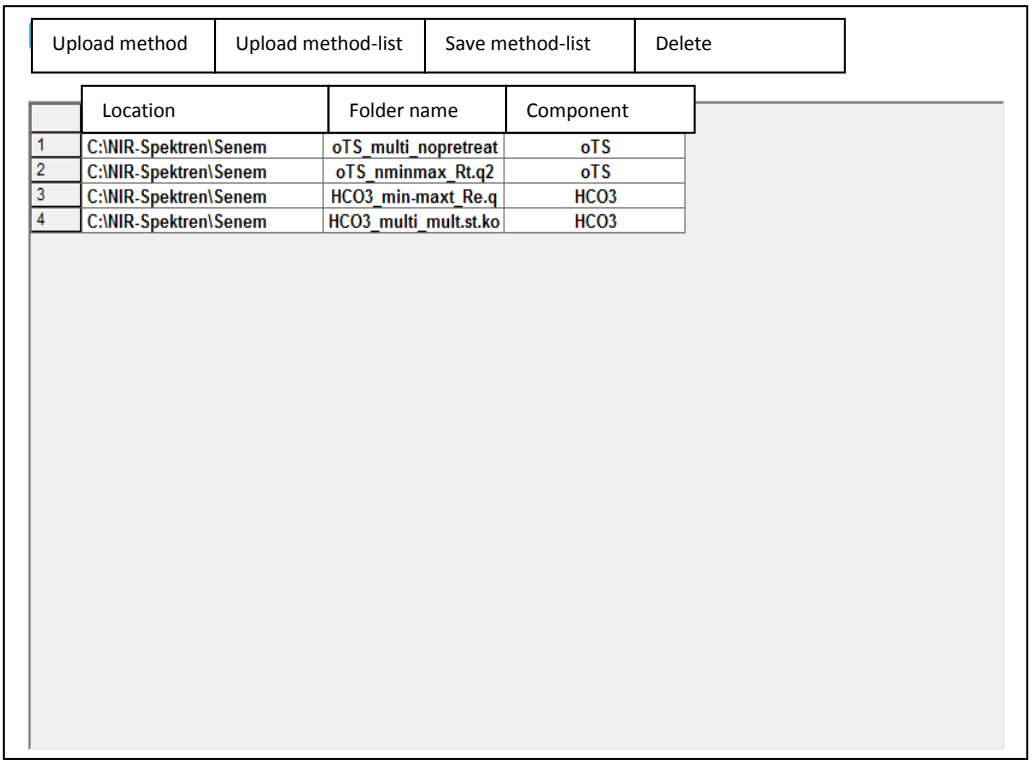

Figure 5.22: The dialog window for methods.

The all spectras, which were analysed, uploaded in dialog window (Figure 5.23). After that, they analysed in three parallels by NIR.

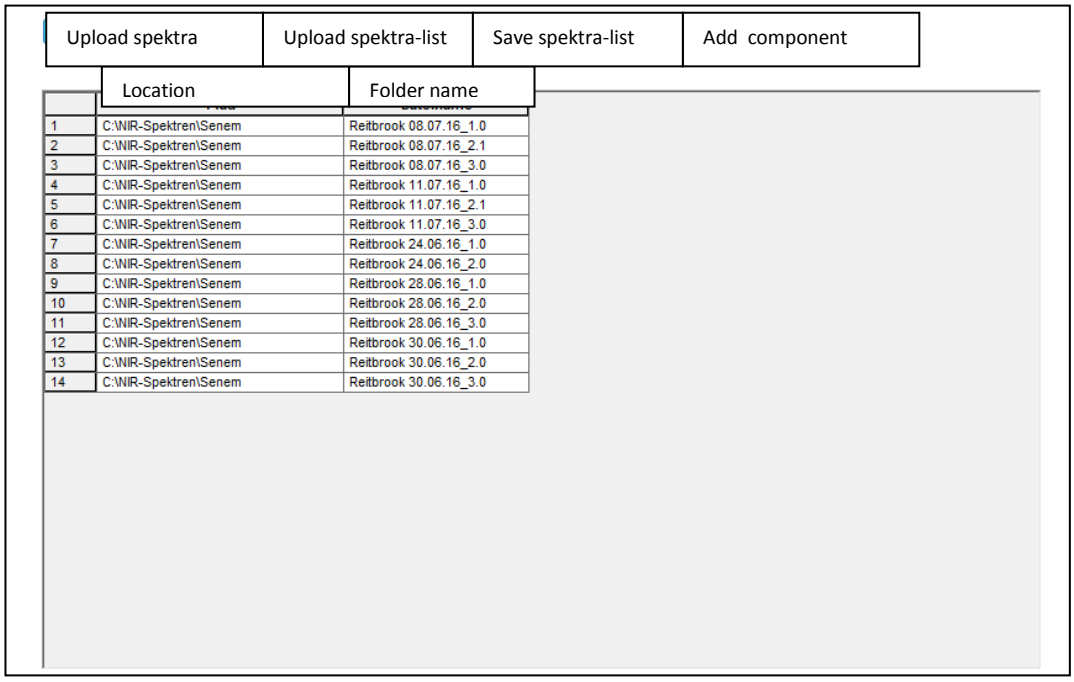

Figure 5.23: The dialog window for spectras.

As can be seen in Figure below (Figure 5.24), the test predictions were given in a table with red mark (which has big difference from other predictions).

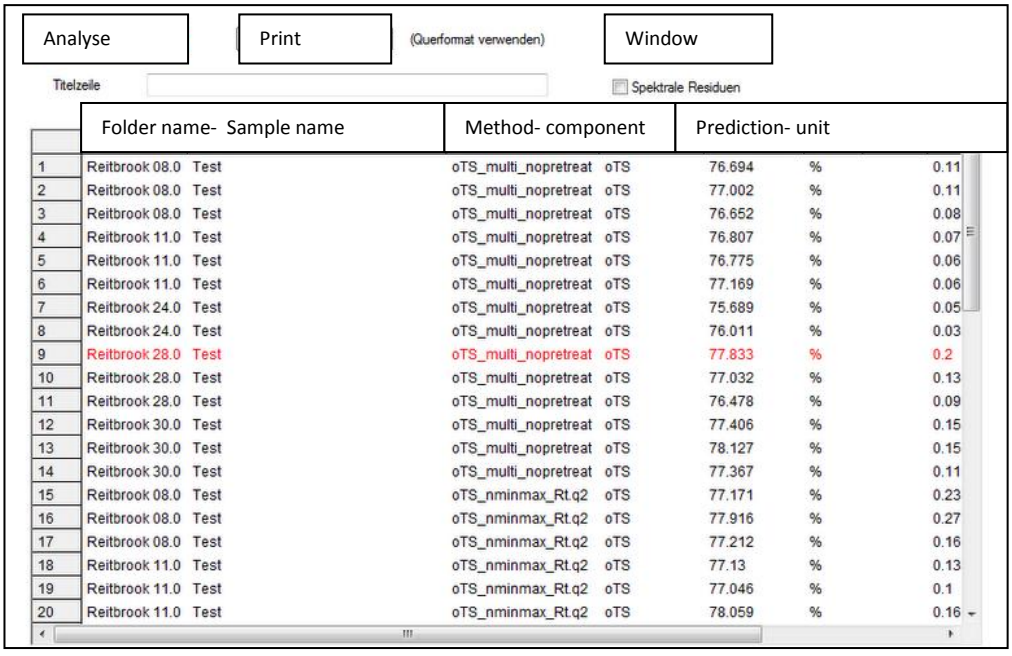

Figure 5.24: Results of test by NIR.

In Table below (Table 5.4), test results of calibration model were explained.

Table 5.4: Test results of calibration model.

Number of sample	Sample abbreviation	Parameter	Mesured average value	Reference value
1	Re.04.03.	DM (%)	1.436 ± 0.2 %	1.63
2	Re.04.03	oDM (%)	71.74 ± 1.2 %	72.59
3	Re.04.03	HCO_3^- (mg/L)	17291.33 ± 483	-
4	Re.04.03	NH_4-N (mg/L)	3191.633 ± 235	-
5	Re.04.03	TN_{CD} (g/L)	4.7059 ± 0.35	-

6. FURTHER RESEARCH PROSPECTS

6.1. Calibration Model Establishment (Multi)

In order to use one calibration model for several biogas plants, new calibration models were conducted by previous researches. The datas were taken from Development of Methodology for monitoring of the Process Stability at Biogas Plant Using Near-Infrared Spectroscopy, which was presented at Eurasia 2016 Waste Management Symposium [26]. The aim of this work is spread application of NIR Spectroscopy with same calibration model for the several biogas plants. This application supplies fast analyse of DM, oDM and HCO_3^-. According to Jacobi, NIR Spectrometer can connect to upstream section of central pipe system. This document explains monitoring of VFA, acetic acid (Hac) and propionig acid (Hpr) [27]. In addition to these parameters, this technology can be used for DM, oDM, HCO_3^-, NH_4-N and VFA monitoring, which prevent time consumption for laboratory analyses. On the other hand, this application supplies fast analyses, easy monitoring oppurtinuty and early intervantion to biogas plant operation.

In addition to that, increases of NIR spectroscopy application decreases chemical consumption for laboratory analyses for all of these parameters. As mentioned before, just small amount of sample is enough to analyse samples by NIR spectroscopy and this measurement does not affect to samples physical and chemical features.

According to Stockl, applicable NIR Calibrations are available for propionic acid and acetic acid in both mesophilic and thermophilic conditions [28]. For acetic acid, RPD of 3.21 in mesophilic conditions and RPD of 4.91 in thermophilic conditions were obtained. In order to use NIR Spectroscopy as online methode, sensors (Figure 6.1) were placed in pipeline and they were connected to NIR spectrometer with fiber optics.

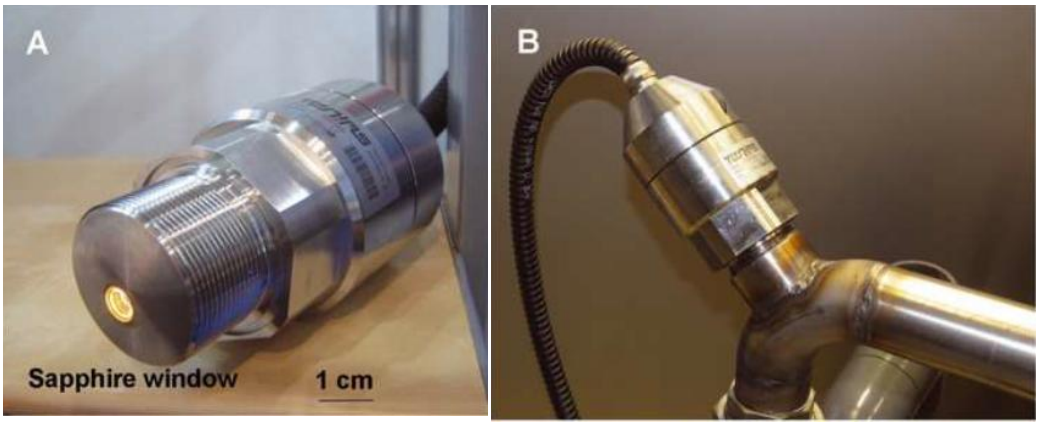

Figure 6.1: Used sensors with display of size and place.

In order to establish a new DM calibration model for Reitbrook and Aldesdorf Biogas Plants samples, multiplicative scatter pretreatment method was applied. As can be seen in Figure below (Figure 6.2), this model has correlation coefficient of 90.04 % and RPD of 3.18. As a result of all these results and report in Table C.1 this model can be used for screening property estimations.

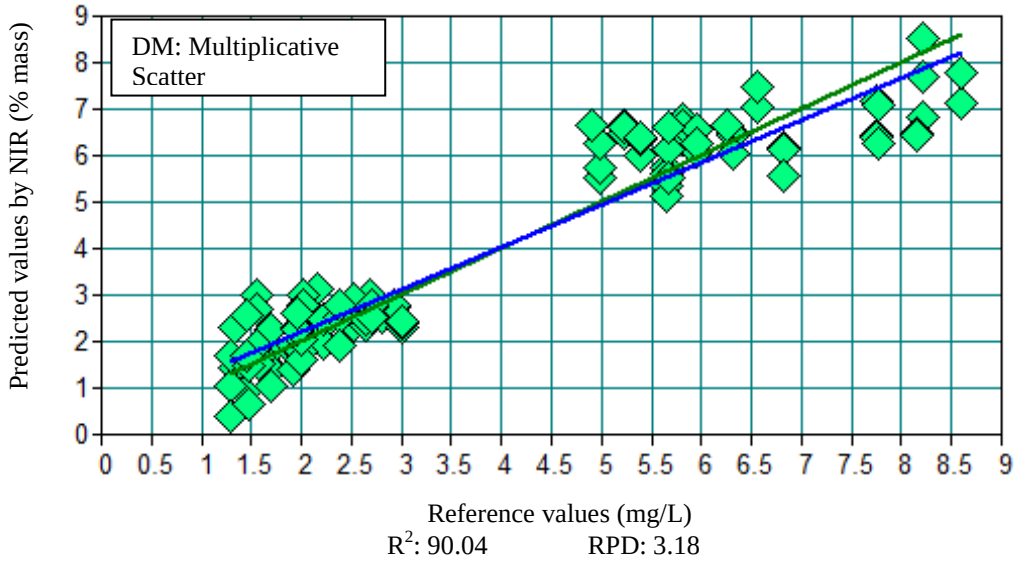

Figure 6.2: Calibration model (multi) for DM - Multiplicative scatter.

The best calibration model for oDM was obtained without pretreatment and report is given in Table C.7. As shown in Figure below (Figure 6.3), this model has correlation coefficient of 80.98 % and RPD of 2.29. Depend on RPD, application of this model is not recommended and need to be developed further.

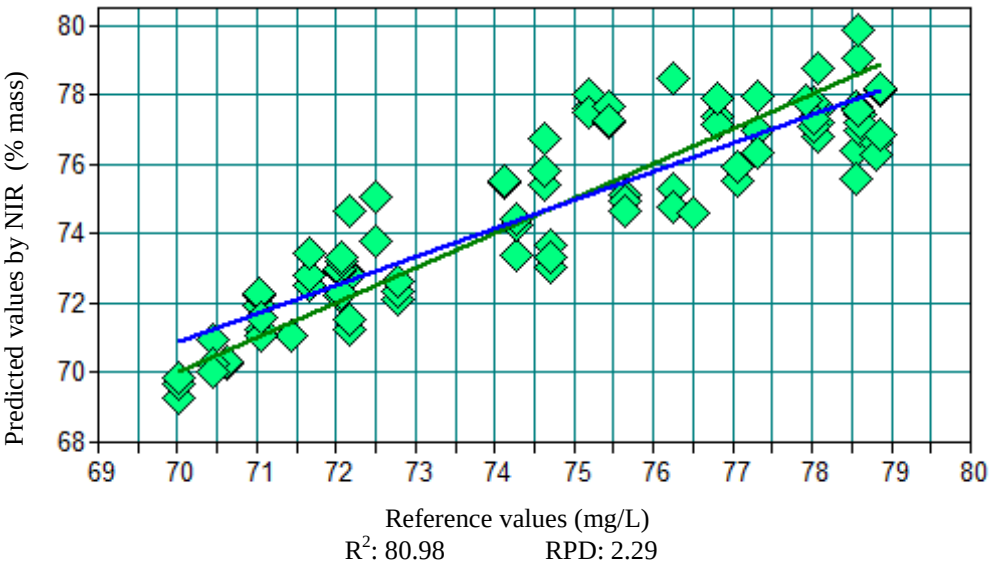

Figure 6.3: Calibration model (multi) for oDM - Without Pretreatment.

Calibration model for HCO_3^- was obtained with multiplicative scatter pretreatment method as shown in Figure 6.4. This model has best correlation coefficient of 81.15 % and 2.3 of RPD. With 2.3 of RPD, this model is not recommended to use. More information can be found in Table C.8.

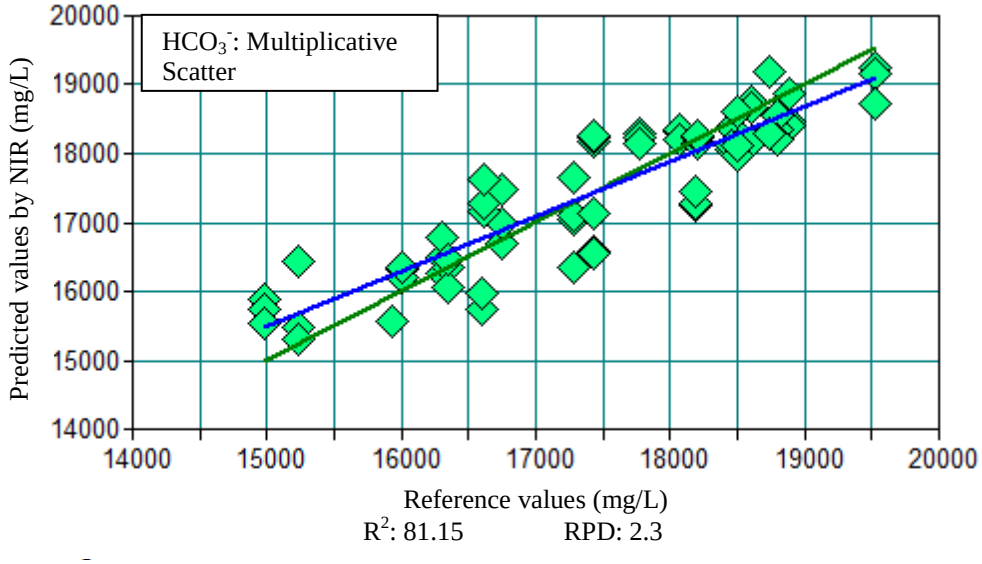

Figure 6.4: Calibration model for HCO3- – Multiplicative Scatter.

6.1.1. Test of calibration model

Calibration model (multi) was also tested as explained before for first calibration model. First of all, methods were uploaded to dialog window for DM, oDM and HCO_3^-. Results of test for multi calibration model are given in Table 6.1.

Table 6.1: Test results of multi calibration model test.

Number of sample	Sample abbreviation	Parameter	Mesured average value	Reference value
1	Re.04.03.	DM (%)	1.728 ± 0.25	1.63
2	Re.04.03	oDM (%)	72.025 ±1.17	72.59
3	Re.04.03	HCO_3^- (mg/L)	16314.66 ± 414.2	-

5 of Reitbrook Biogas Plant samples, which were not used for calibration model establishment, tested by NIR with both single and multi calibration models. The test was applied for HCO_3^- and oDM parameters. All results are given in Table below (Table 6.2).

Based on differences between referance measured average values and reference values, better results were obtained with "oDM_multi_nopretreatment" method for oDM test. Although with "HCO3_multi_mult.st" method better results were obtained for HCO_3^-, the difference between two methods is not much to be considered.

As a general result of all calibration models, they can be used for at least for the roughly property estimation which is already sufficient for the objectives of at-line monitoring. However, in order to improve statistical performance of the model, more samples need to be included.

Table 6.2: Test results of calibration model (multi and single).

Number of sample	Sample abbreviation	Parameter	Method	Measured average value	Reference value
1	Re.08.07	oDM (%)	oDM_multi_nopretreatment	76.782 ±0,15	77.886
			oDM_nminmax_Rt	77.433 ±0.31	
2	Re.11.07	oDM (%)	oDM_multi_nopretreatment	76,917 ±0,17	77.250
			oDM_nminmax_Rt	77.412 ±0.45	
3	Re.24.06	oDM (%)	oDM_multi_nopretreatment	75.850 ±0.13	77.050
			oDM_nminmax_Rt	75.774 ±0.11	
4	Re.28.06	oDM (%)	oDM_multi_nopretreatment	77.114 ±0.55	77.310
			oDM_nminmax_Rt	78.214 ±0.63	
5	Re.30.06	oDM (%)	oDM_multi_nopretreatment	77.733 ±0.31	77.820
			oDM_nminmax_Rt	78.560 ±0.39	
6	Re.08.07	HCO_3^- (mg/L)	HCO3_min-maxt_Rt	14590 ±364	15425
			HCO3_multi_mult.st	16069 ±129	
7	Re.11.07	HCO_3^- (mg/L)	HCO3_min-maxt_Rt	15847 ±109	15327
			HCO3_multi_mult.st	16469 ±31	
8	Re.24.06	HCO_3^- (mg/L)	HCO3_min-maxt_Rt	16083 ±229	15669
			HCO3_multi_mult.st	16943 ±37	
9	Re.28.06	HCO_3^- (mg/L)	HCO3_min-maxt_Rt	14451 ±357	15620
			HCO3_multi_mult.st	15828 ±308	
10	Re.30.06	HCO_3^- (mg/L)	HCO3_min-maxt_Rt	13764 ±574	14985
			HCO3_multi_mult.st	15992 ±85	

6.2. Suggestion of New Substrate – Sugar beets

Substrate type and composition affects to biogas production rate of digerstion process and methane content of biogas. Necassary rate of C:N:P:S for biogas production in anaerobic digestion proccess is 600:15:5:3 [29]. In order to test usability of sugar beets as a new substrate, biogas potential of sugar beets were tested

with GB_{21} test as applied for pellets. Biogas generation volumes were recorded during 24 days and accumulated biogas generation calculated within experiment period. Results for the three parallel tests aregiven in Figure below (Figure 6.5).

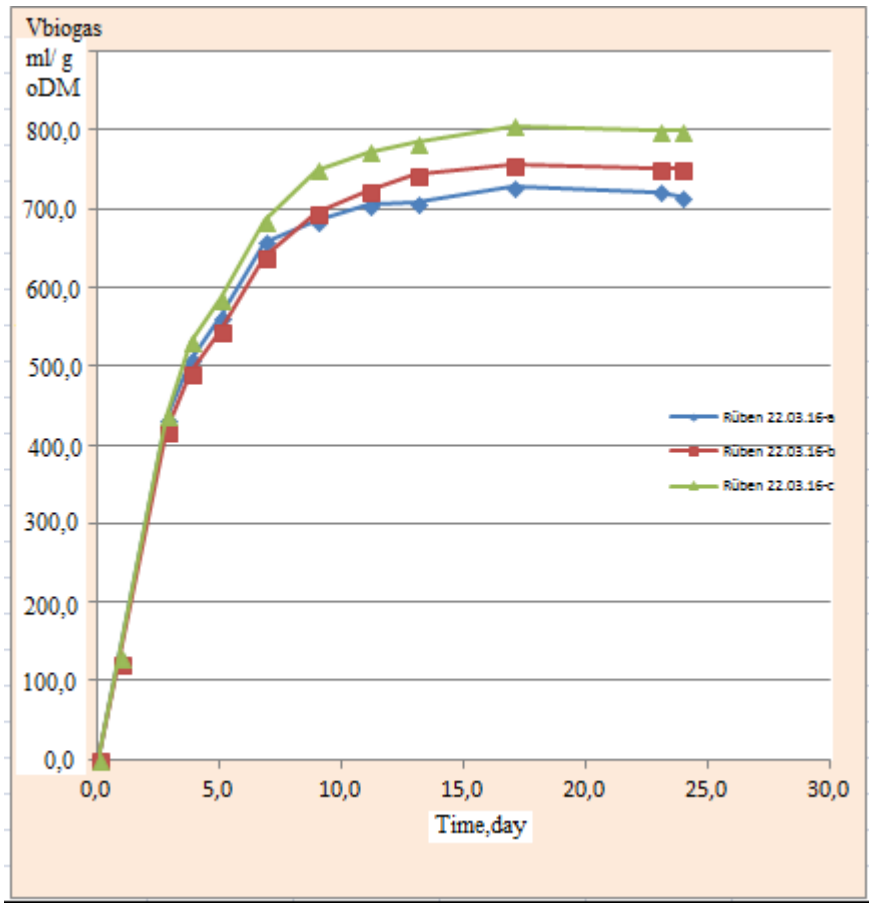

Figure 6.5: Results of biogas potential test for sugar beets.

Based on biogas potential of sugar beets and pellets, the extensive comparision informations were given in Table 6.3. As can be seen in Table below (Table 6.3), sugar beets have biogas potential more than pellets per organic dry matter.

Table 6.3: Comparision of biogas potential results for sugar beets and pellets.

	Result of Pellets	**Results of Sugar beets**	**Unit**
Per wet matter (FM)	582.5 ± 47.14	124.9 ± 6.5	$ml_N.(g\ FM)^{-1}$
Per dry matter (DM)	673.8 ±55.47	626.4 ± 34.46	$ml_N.(g\ DM)^{-1}$
Per organic dry matter (oDM)	692.4 ± 57.67	763.4 ±43.07	$ml_N.(g\ oDM)^{-1}$
DM content of substrate	86.45	19.94	% DM
oDM content of substrate	97.31	82.06	% oDM

Accorting to Hassan [29], sugar beets sludge has 90 % degradation efficiency. It was obtained by experiments that sugar beets sludge has stabil 53 % biogas content and lincludes less than 100 ppm H_2S. With addition of cow manure as substrate efficiency of biogas production can be increased [29]. Although sugar beets have high biogas potential, they have high water content. That makes difficult to handle substrate, which means additional storage features are needed. The optimizing of expenses for additional construction and incomes from biogas is necessary.

7. CONCLUSION

The energy demand of world increases quickly day by day. Literature rewiev shows that, there is a big tendency to extend usage of renewable energy all over the world. In order to decrease emission of green house gases and evaluate wastes as a source, biogas production by anaerobic digestion technology is getting popular in Europa and other countries. Despite Germany has biggest number of biogas plants and most improved biogas production technology, there is still a need to improve monitoring systems of biogas plants. NIR (Near Infrared) spectroscopy gives an oppurtunity to monitor biogas plant in quick and reliable way.

The Pilot Scale Biogas Plant in Reitbrook (has 1.5 m^3 net digestate volume) was successfully operated during 120 days in mesophilic conditions. Feeding was conducted manually with changes of amount in periods from 1.5 kg to 4.5 kg. Pellets were used as substrate, which have high content of organic matter.

The strategy of biogas plant monitoring based on daily, weekly, monthly and yearly controls of specified parameters. Monitoring of biogas plant consists of on-line monitoring of temperature, pressure, gas production volume and self energy consumption amount; off-line monitoring of DM, oDM, pH, FOS/TAC, NH_4-N, TN_{CD}, VFA and HCO_3^- in laboratory; improvement of at-line monitoring system for all these parameters with single and multi calibration models. Within operation period value of parameters changed with the effect of changes in feeding amount and some technical problems. Effective operational problems were organic overload and heating system failure at fermenter. Daily biogas production fluctated between 0.133 m^3 and 1.192 m^3 with average 43 % average CH_4 content. Gas content analyses were conducted by mobile gas analyser at biogas plant and gas chromotography at the laboratory. For laboratory analyses, samples were taken weekly. DM % increased from 1.57 % to 3 %; oDM % increased from 71.04 % to 76.88 %; pH value fluctated between 7.03 and 8.06; FOS/TAC increased from 0.132 to 1.73; NH_4-N concentration fluctated between 2921 mg/L and 4394 mg/L; range of TN_{CD} concentration was between 4.8 g/L – 6.8 g/L; concentration of VFA increased from

73 mg/L to 13865 mg/L; HCO_3^- concentration fluctated between 14985 mg/L and 20550 mg/L.

In order to evaluate availability of different substrates, pellets were tested both in biogas plant and in laboratory with implementation of calorific value test, which can give an idea for the comparision of incineration and digestion technology. In addition that, biogas production capacity of pellets was tested with GB_{21} test at laboratory scale. For further research prospects, in addition to pellets, biogas potential of sugar beets was tested in laboratory scale with implementation of GB_{21} test.

The main aim of thesis was developing of NIR spectroscopy applicability as online monitoring system. 24 random selected digestate samples from biogas plant were used to create a calibration model for parameters, which are generally analysed at laboratory. In order to prevent time consumption for long laboratory analyses and have an oppurtinuty to quicker intervention to fermenter parameters, application of NIR specroscopy have significant place in biogas plant development investigations. For DM, oDM, TN_{CD}, VFA, NH_4-N and HCO_3^-, calibration models were developed.

Calibration models were evaluated based on correlation coefficient and value of RPD. The best calibration model was obtained for DM analyses with 94.81 % of R^2 and 4.39 of RPD without pretreatment. This model can be used for screening property estimations. Other calibration models, which were obtained for other parameters, most of them can be used for roughly estimations. That supplies to quick information about increases and decreases of parameters. In order to improve calibration models for further researches, more samples are needed.

Such a calibration, which can be used for roughly estimations, it is still recommended to use for on-line monitoring developments. During research part of thesis, NIR spectroscopy was applied as an at-line technology. That means, although it is not quicker as on-line monitoring, it gives quicker results than laboratory analyses. As a result of all these informations, it is possible to implement NIR spectroscopy as an on-line monitoring system of biogas plant for various parameters.

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APPENDICES

APPENDIX A: Operation Informations of Biogas Plant
APPENDIX B: Results of Labaratory Analyses
APPENDIX C: Calibration Model Establishment with NIR Spectroscopy

APPENDIX A: Operation Informations of Biogas Plant

Table A. 1: Daily records of feeding amount, biogas and CH_4 production at biogas. plant

Date	Operation Day	Feeding, kg	OLR (Organic Loading Rate)	Biogas production, m^3/day	Biogas production, accumulated m^3	CH_4 production m^3/day	CH4 production, accumulated m^3
08.03.16	0	0	0,000	0,000	0,000	0,000	0,000
09.03.16	1	2	1,333	0,133	0,133	0,061	0,061
10.03.16	2	0	1,333	0,252	0,386	0,116	0,177
11.03. 16	3	2	1,333	0,252	0,638	0,116	0,293
13.03. 16	4	0	1,333	0,003	0,641	0,001	0,294
14.03. 16	5	2	1,333	0,003	0,644	0,001	0,295
15.03. 16	6	2	1,333	0,003	0,646	0,001	0,296
16.03. 16	7	2	1,333	0,003	0,649	0,001	0,298
17.03. 16	8	2	1,333	0,477	1,126	0,219	0,516
18.03.16	9	2	1,333	0,841	1,967	0,386	0,902
19.03.16	10	0	1,333	0,494	2,461	0,227	1,129
20.03.16	11	0	1,333	0,292	2,753	0,134	1,262
21.03.16	12	0	1,333	0,292	3,045	0,134	1,396
22.03.16	13	0	2,000	0,292	3,337	0,134	1,530
23.03.16	14	3	2,000	0,292	3,628	0,134	1,664
24.03.16	15	0	2,000	0,292	3,920	0,134	1,798
25.03.16	16	3	2,000	0,292	4,212	0,134	1,932
26.03.16	17	0	2,000	0,292	4,504	0,134	2,066
27.03.16	18	0	2,000	0,216	4,720	0,099	2,165
28.03.16	19	3	2,000	0,216	4,937	0,099	2,264
29.03.16	20	3	2,000	0,216	5,153	0,099	2,363
30.03.16	20	3	2,000	0,216	5,369	0,099	2,462
31.03.16	22	3	2,000	0,499	5,868	0,229	2,691
01.04.16	23	3	2,000	0,884	6,752	0,405	3,097
02.04.16	24	0	2,000	0,974	7,726	0,447	3,543
03.04.16	25	0	2,000	0,753	8,479	0,345	3,888
04.04.16	26	3	2,000	0,753	9,231	0,345	4,234
05.04.16	27	3	2,000	0,753	9,984	0,345	4,579
06.04.16	28	3	2,000	0,800	10,784	0,367	4,946
07.04.16	29	3	2,000	0,800	11,584	0,367	5,313
08.04.16	30	0	2,000	1,192	12,776	0,547	5,859
09.04.16	31	0	2,000	0,877	13,653	0,402	6,262
10.04.16	32	0	2,000	0,877	14,531	0,402	6,664
11.04.16	33	3	2,000	0,877	15,408	0,402	7,066
12.04.16	34	0	2,000	0,877	16,285	0,402	7,469
13.04.16	35	3	2,000	0,614	16,899	0,282	7,750
14.04.16	36	3	2,000	0,614	17,513	0,282	8,032
15.04.16	37	3	2,000	0,589	18,102	0,270	8,302

16.04.16	38	0	2,000	1,219	19,321	0,559	8,861
17.04.16	39	0	2,000	0,762	20,083	0,350	9,211
18.04.16	40	3	2,000	0,762	20,846	0,350	9,560
19.04.16	40	3	2,000	0,762	21,608	0,350	9,910
20.04.16	42	3	2,000	0,703	22,311	0,322	10,232
21.04.16	43	3	2,000	0,734	23,045	0,337	10,569
22.04.16	44	0	2,000	0,291	23,336	0,133	10,702
23.04.16	45	0	2,000	1,392	24,728	0,638	11,341
24.04.16	46	0	2,000	0,546	25,274	0,250	11,591
25.04.16	47	3	2,000	0,546	25,819	0,250	11,841
26.04.16	48	3	2,000	0,546	26,365	0,250	12,091
27.04.16	49	3	2,000	0,546	26,911	0,250	12,342
28.04.16	50	3	2,000	0,546	27,456	0,250	12,592
29.04.16	51	3	2,000	0,546	28,002	0,250	12,842
30.04.16	52	0	2,000	0,706	28,708	0,324	13,166
01.05.16	53	0	2,000	0,706	29,414	0,324	13,489
02.05.16	54	3	2,000	0,706	30,119	0,324	13,813
03.05.16	55	3	2,000	0,706	30,825	0,324	14,137
04.05.16	56	3	2,000	0,609	31,434	0,279	14,416
05.05.16	57	0	2,000	0,896	32,330	0,411	14,827
06.05.16	58	3	2,000	0,776	33,107	0,356	15,183
07.05.16	59	0	2,000	0,776	33,883	0,356	15,539
08.05.16	60	0	2,000	0,567	34,450	0,260	15,799
09.05.16	60	3	2,000	0,567	35,018	0,260	16,060
10.05.16	62	0	2,000	0,567	35,585	0,260	16,320
11.05.16	63	0	2,000	1,105	36,690	0,507	16,826
12.05.16	64	3	2,000	1,105	37,795	0,507	17,333
13.05.16	65	3	2,000	1,105	38,899	0,507	17,840
14.05.16	66	0	2,000	1,105	40,004	0,507	18,346
15.05.16	67	0	2,000	0,669	40,673	0,307	18,653
16.05.16	68	3	2,000	0,669	41,341	0,307	18,960
17.05.16	69	3	2,000	0,669	42,010	0,307	19,266
18.05.16	70	3	2,000	0,733	42,743	0,336	19,603
19.05.16	71	3	2,000	0,690	43,433	0,316	19,919
20.05.16	72	3	2,000	0,322	43,755	0,147	20,066
21.05.16	73	0	2,000	0,322	44,076	0,147	20,214
22.05.16	74	0	2,000	0,313	44,389	0,143	20,357
23.05.16	75	3	2,000	0,313	44,701	0,143	20,501
24.05.16	76	0	2,000	0,313	45,014	0,143	20,644
25.05.16	77	0	2,000	0,197	45,211	0,090	20,734
26.05.16	78	0	2,000	0,197	45,408	0,090	20,825
27.05.16	79	3	2,000	0,197	45,605	0,090	20,915
28.05.16	80	0	2,000	0,298	45,903	0,137	21,052
29.05.16	80	0	2,000	0,354	46,257	0,162	21,214
30.05.16	82	3	2,000	0,354	46,610	0,162	21,376
31.05.16	83	0	2,000	0,354	46,964	0,162	21,538

01.06.16	84	0	2,000	0,267	47,231	0,122	21,661
02.06.16	85	0	2,000	0,267	47,498	0,122	21,783
03.06.16	86	3	2,000	0,267	47,764	0,122	21,905
04.06.16	87	0	2,000	0,267	48,031	0,122	22,028
05.06.16	88	0	2,000	0,327	48,358	0,150	22,178
06.06.16	89	3	2,000	0,327	48,685	0,150	22,328
07.06.16	90	3	2,667	0,327	49,012	0,150	22,478
08.06.16	91	4	2,667	0,216	49,228	0,099	22,577
09.06.16	92	4	2,667	0,360	49,588	0,165	22,742
10.06.16	93	4	2,667	0,601	50,189	0,190	15,872
11.06.16	94	0	2,667	0,575	50,764	0,182	16,054
12.06.16	95	0	2,667	0,565	51,329	0,179	16,233
13.06.16	96	4	2,667	0,565	51,894	0,179	16,411
14.06.16	97	4	2,667	0,565	52,459	0,179	16,590
15.06.16	98	4	2,667	0,692	53,151	0,219	16,809
16.06.16	99	0	2,667	0,215	53,366	0,068	16,877
17.06.16	100	4	2,667	0,584	53,950	0,185	17,062
18.06.16	100	0	2,667	0,584	54,534	0,185	17,246
19.06.16	102	0	3,000	0,593	55,127	0,291	27,067
20.06.16	103	4,5	3,000	0,593	55,719	0,291	27,358
21.06.16	104	4,5	3,000	0,593	56,312	0,291	27,649
22.06.16	105	4,5	3,000	0,484	56,796	0,238	27,887
23.06.16	106	4,5	3,000	0,484	57,280	0,238	28,124
24.06.16	107	4,5	0,000	0,489	57,769	0,145	17,080
25.06.16	108	0	0,000	0,500	0,000	0,148	17,228
26.06.16	109	0	0,000	0,115	0,115	0,034	17,262
27.06.16	110	0	0,000	0,151	0,267	0,045	17,307
28.06.16	111	0	0,000	0,118	0,385	0,035	17,342
29.06.16	112	0	0,000	0,460	0,845	0,136	17,478
30.06.16	113	0	0,000	0,606	1,451	0,179	17,657
01.07.16	114	0	0,000	0,472	1,923	0,140	17,797
02.07.16	115	0	0,000	0,570	2,493	0,169	17,965
03.07.16	116	0	0,000	0,878	3,371	0,260	18,225
04.07.16	117	0	0,000	0,878	4,250	0,260	18,485
05.07.16	118	0	0,000	0,396	4,645	0,115	18,599
06.07.2016	119	0	0,000	0,396	5,041	0,115	18,714

Table A. 2: Results of Gas Composition Analyses.

Date	Operation day	CH4, %	CO_2, %	O_2, %	H_2S, ppm	N_2, %
08.03.2016	0	46	42,2	1,6	344	10,2
11.04.2016	34	49,5	38,3	1,6	366	10,6
15.04.2016	38	46,637253	45,819967	1,639866	463	5,902914
21.04.2016	44	41,9	45,3	1,9	387	10,9
28.04.2016	51	49,3	45,7	0,3	506	4,7
12.05.2016	65	43,3	48,3	0,9	434	7,5
13.05.2016	66	45,2	47,7	0,4	406	6,6
18.05.2016	71	45,2	43,6	1,3	409	9,9
19.05.2016	72	45,9	45,8	0,7	336	7,6
20.05.2016	73	46,1	47,8	0,4	415	5,8
26.05.2016	79	48,2	46,6	0,2	415	5
06.06.2016	90	41,3	36,4	2,8	229	19,5
08.06.2016	92	47,8	47,8	0,2	437	4,2
09.06.2016	93	30,2	64,6	0,5	381	4,8
10.06.2016	94	28,6	65	0,8	346	5,5
15.06.2016	99	31,1	58,5	1,3	567	9,1
17.06.2016	101	36,6	57,8	0,5	898	5
20.06.2016	104	49,1	40,8	0,8	801	9,3
23.06.2016	107	28,1	64,3	0,7	660	6,8
01.07.2016	115	25,5	66,8	1,2	638	6,5
04.07.2016	117	35,1	53	1,4	729	10,5
07.07.2016	120	46,3	44,4	0,8	741	8,5

Table A. 3: Daily and Accumulated; Energy Consumption and production.

Date	Operation Day	Energy Consumption kWh/day	Energy Production kwh/day	Accumulated Energy Consumption kWh	Accumulated Energy Production kWh
08.03.2016	0	0	0	0	0
09.03.2016	1	24,01	0,80	24,0	0,8
10.03.2016	2	22,91	1,51	46,9	2,3
11.03.2016	3	22,81	1,51	69,7	3,8
12.03.2016	4	23,01	0,02	92,7	3,8
13.03.2016	5	25,4	0,02	118,1	3,9
14.03.2016	6	21,42	0,02	139,6	3,9
15.03.2016	7	23,6	0,02	163,2	3,9
16.03.2016	8	25,7	2,86	188,9	6,8
17.03.2016	9	19,93	5,05	208,8	11,8
18.03.2016	10	23,4	2,96	232,2	14,8
19.03.2016	11	21,42	1,75	253,6	16,5
20.03.2016	12	22,01	1,75	275,6	18,3
21.03.2016	13	22,02	1,75	297,6	20,0
22.03.2016	14	20,62	1,75	318,3	21,8
23.03.2016	15	20,02	1,75	338,3	23,5
24.03.2016	16	19,83	1,75	358,1	25,3
25.03.2016	17	21,81	1,75	379,9	27,0
26.03.2016	18	19,72	1,30	399,6	28,3
27.03.2016	19	19,83	1,30	419,5	29,6
28.03.2016	20	21,51	1,30	441,0	30,9
29.03.2016	21	19,62	1,30	460,6	32,2
30.03.2016	22	20,03	2,99	480,6	35,2
31.03.2016	23	18,42	5,30	499,1	40,5
01.04.2016	24	18,43	5,84	517,5	46,4
02.04.2016	25	16,94	4,52	534,4	50,9
03.04.2016	26	14,34	4,52	548,8	55,4
04.04.2016	27	13,75	4,52	562,5	59,9
05.04.2016	28	17,73	4,80	580,2	64,7
06.04.2016	29	18,43	4,80	598,7	69,5
07.04.2016	30	27,02	7,15	625,7	76,7
08.04.2016	31	19,62	5,26	645,3	81,9
09.04.2016	32	18,43	5,26	663,7	87,2
10.04.2016	33	17,63	5,26	681,4	92,4
11.04.2016	34	22,41	5,26	703,8	97,7
12.04.2016	35	16,73	3,68	720,5	101,4
13.04.2016	36	15,44	3,68	736,0	105,1
14.04.2016	37	18,13	3,53	754,1	108,6
15.04.2016	38	17,13	7,31	771,2	115,9
16.04.2016	39	19,03	4,57	790,2	120,5
17.04.2016	40	18,83	4,57	809,1	125,1

18.04.2016	41	18,62	4,57	827,7	129,6
19.04.2016	42	20,23	4,22	847,9	133,9
20.04.2016	43	20,12	4,40	868,0	138,3
21.04.2016	44	18,52	1,75	886,6	140,0
22.04.2016	45	20,82	8,35	907,4	148,4
23.04.2016	46	21,22	3,27	928,6	151,6
24.04.2016	47	21,91	3,27	950,5	154,9
25.04.2016	48	21,92	3,27	972,4	158,2
26.04.2016	49	37,65	3,27	1010,1	161,5
27.04.2016	50	55,38	3,27	1065,5	164,7
28.04.2016	51	-	3,27	1065,5	168,0
29.04.2016	52	-	4,23	1065,5	172,2
30.04.2016	53	50,6	4,23	1116,1	176,5
01.05.2016	54	48,2	4,23	1164,3	180,7
02.05.2016	55	49,7	4,23	1214,0	185,0
03.05.2016	56	-	3,65	1214,0	188,6
04.05.2016	57	51,3	5,38	1265,3	194,0
05.05.2016	58	-	4,66	1265,3	198,6
06.05.2016	59	-	4,66	1265,3	203,3
07.05.2016	60	46,8	3,40	1312,1	206,7
08.05.2016	61	-	3,40	1312,1	210,1
09.05.2016	62	-	3,40	1312,1	213,5
10.05.2016	63	46,5	6,63	1358,6	220,1
11.05.2016	64	46,7	6,63	1405,3	226,8
12.05.2016	65	-	6,63	1405,3	233,4
13.05.2016	66	-	6,63	1405,3	240,0
14.05.2016	67	57,6	4,01	1462,9	244,0
15.05.2016	68	58,8	4,01	1521,7	248,0
16.05.2016	69	37,9	4,01	1559,6	252,1
17.05.2016	70	18,37	4,40	1577,9	256,5
18.05.2016	71	16,6	4,14	1594,5	260,6
19.05.2016	72	-	1,93	1594,5	262,5
20.05.2016	73	-	1,93	1594,5	264,5
21.05.2016	74	14	1,88	1608,5	266,3
22.05.2016	75	-	1,88	1608,5	268,2
23.05.2016	76	-	1,88	1608,5	270,1
24.05.2016	77	0,8	1,18	1609,3	271,3
25.05.2016	78	-	1,18	1609,3	272,4
26.05.2016	79	-	1,18	1609,3	273,6
27.05.2016	80	-	1,79	1609,3	275,4
28.05.2016	81	-	2,12	1609,3	277,5
29.05.2016	82	-	2,12	1609,3	279,7
30.05.2016	83	-	2,12	1609,3	281,8
31.05.2016	84	-	1,60	1609,3	283,4
01.06.2016	85	14,54	1,60	1623,9	285,0
02.06.2016	86	27,99	1,60	1651,9	286,6

03.06.2016	87	44,02	1,60	1695,9	288,2
04.06.2016	88	42,54	1,96	1738,4	290,1
05.06.2016	89	46,42	1,96	1784,8	292,1
06.06.2016	90	43,03	1,96	1827,9	294,1
07.06.2016	91	43,82	1,30	1871,7	295,4
08.06.2016	92	29,19	2,16	1900,9	297,5
09.06.2016	93	3,59	3,61	1904,5	301,1
10.06.2016	94	4,08	3,45	1908,6	304,6
11.06.2016	95	3,49	3,39	1912,0	308,0
12.06.2016	96	3,78	3,39	1915,8	311,4
13.06.2016	97	3,19	3,39	1919,0	314,8
14.06.2016	98	30,18	4,15	1949,2	318,9
15.06.2016	99	11,65	1,29	1960,8	320,2
16.06.2016	100	19,23	3,50	1980,1	323,7
17.06.2016	101	10,26	3,50	1990,3	327,2
18.06.2016	102	1,29	3,56	1991,6	330,8
19.06.2016	103	1,2	3,56	1992,8	334,3
20.06.2016	104	0,983078	3,56	1993,8	337,9
21.06.2016	105	0,98299	2,90	1994,8	340,8
22.06.2016	106	35,96	2,90	2030,7	343,7
23.06.2016	107	19,33	2,93	2050,1	346,6
24.06.2016	108	1,09	3,00	2051,2	349,6
25.06.2016	109	1,5	0,69	2052,7	350,3
26.06.2016	110	1,29	0,91	2054,0	351,2
27.06.2016	111	1	0,71	2055,0	351,9
28.06.2016	112	0,99	2,76	2055,9	354,7
29.06.2016	113	1	3,64	2056,9	358,3
30.06.2016	114	1,2	2,83	2058,1	361,2
01.07.2016	115	19,22	3,42	2077,4	364,6
03.07.2016	116	35,66	5,27	2113,0	369,8
04.07.2016	117	36,35	5,27	2149,4	375,1
05.07.2016	118	35,37	2,37	2184,7	377,5
06.07.2016	119	34,67	2,37	2219,4	379,9
07.07.2016	120	34,57		2254,0	379,9

APPENDIX B: Results of Labaratory Analyses

Table B. 1: Results of Laboratory Analyses; DM, oDM, pH, FOS/TAC, NH_4-N, TN CD, VFA, HCO_3.

Date	Operation Day	DM, %	oDM, %	pH	FOS/TAC	NH_4-N, mg/L	TN_{CD}, g/L	VFA, mg/L	HCO_3, mg/L
11.03.2016	3	1,57	71,04	8,06	0,132	3624	4,95	73	17426
18.03.2016	10	1,56	71,65	7,85	0,261	3361	4,91	491	16621
06.04.2016	29	1,69	72,17	7,92	0,162	3330	5	570	17280
15.04.2016	38	1,85	73,65	7,87	0,163	3001	4,8	810	17743
21.04.2016	44	1,95	72,065	7,888	0,158	2921	5,13	934	18183
06.05.2016	59	2,01	72,487	7,94	0,146	4168	5,21	439	19208
12.05.2016	65	1,92	72,053	7,82	0,167	3644	5,75	840	19037
20.05.2016	73	2	72,78	7,83	0,205	3929	5,45	792	19476
03.06.2016	87	2,15	74,7	7,87	0,1657	3929	5,45	490	20550
10.06.2016	94	2,22	74,27	-	-	3770	5,78	3264	16304
15.06.2016	99	2,69	78,56	7,4	0,785	4196	6,08	5100	16596
17.06.2016	101	2,53	74,63	7,35	0,939	4147	5,61	8318	16743
21.06.2016	105	2,39	75,64	7,26	0,95	3941	6,05	8849	16010
24.06.2016	108	2,64	77,05	6,99	1,36	4394	5,89	10997	15669
28.06.2016	112	2,7	77,31	7,03	1,53	3891	-	12854	15620
30.06.2016	114	3	77,82	6,83	1,85	4009	6,85	13865	14985
08.07.2016	120	2,8	76,8865	7,13	1,73	3945	6,41	13566	15425

APPENDIX C: Calibration Model Establishment with NIR Spectroscopy

Table C. 1: DM – Single Calibration Model Report (Without Pretreatment).

Sample Name	Referans Value	Estimated Value by NIR	Difference
Reitbrook 03.06.16_1.0	2.15	2.075	0.0753
Reitbrook 03.06.16_2.0	2.15	1.978	0.172
Reitbrook 03.06.16_3.0	2.15	2.062	0.0876
Reitbrook 05.02.16_1.0	1.34	1.259	0.0811
Reitbrook 05.02.16_2.0	1.34	1.332	0.00784
Reitbrook 05.02.16_3.0	1.34	1.402	-0.0624
Reitbrook 06.04.16_2.0	1.69	1.727	-0.0371
Reitbrook 06.04.16_2.1	1.69	1.548	0.142
Reitbrook 06.04.16_3.0	1.69	1.711	-0.0214
Reitbrook 06.04.16_3.1	1.69	1.517	0.173
Reitbrook 06.05.16_1.0	2.01	2.247	-0.237
Reitbrook 06.05.16_2.0	2.01	2.025	-0.0153
Reitbrook 06.05.16_3.0	2.01	2.07	-0.0601
Reitbrook 10.06.16_1.0	2.22	2.134	0.0855
Reitbrook 10.06.16_2.0	2.22	2.259	-0.0386
Reitbrook 10.06.16_3.0	2.22	2.232	-0.0119
Reitbrook 11.03.16_1.0	1.57	1.719	-0.149
Reitbrook 11.03.16_2.0	1.57	1.666	-0.0963
Reitbrook 11.03.16_3.0	1.57	1.729	-0.159
Reitbrook 12.05.16_1.0	1.92	1.825	0.0946
Reitbrook 12.05.16_2.0	1.92	1.886	0.0335
Reitbrook 12.05.16_3.0	1.92	1.872	0.0479
Reitbrook 15.06.16_1.0	2.69	2.943	-0.253
Reitbrook 15.06.16_2.0	2.69	2.683	0.00668
Reitbrook 15.06.16_3.0	2.69	2.568	0.122
Reitbrook 16.02.16_1.0	1.43	1.516	-0.0856
Reitbrook 17.06.16_1.0	2.53	2.498	0.0318
Reitbrook 17.06.16_2.0	2.53	2.529	0.00144
Reitbrook 17.06.16_3.0	2.53	2.804	-0.274
Reitbrook 18.03.16_1.0	1.56	1.667	-0.107
Reitbrook 18.03.16_2.0	1.56	1.804	-0.244
Reitbrook 18.03.16_3.0	1.56	1.872	-0.312
Reitbrook 20.05.16_1.0	2	1.994	0.00609
Reitbrook 20.05.16_2.0	2	1.987	0.0131
Reitbrook 20.05.16_3.0	2	2.084	-0.0842
Reitbrook 21.04.16_1.0	1.95	1.72	0.23
Reitbrook 21.04.16_3.0	1.95	1.776	0.174
Reitbrook 21.06.16_1.0	2.39	2.537	-0.147
Reitbrook 21.06.16_2.0	2.39	2.483	-0.0933
Reitbrook 21.06.16_3.0	2.39	2.438	-0.0476
Reitbrook 24.06.16_1.0	2.64	2.518	0.122
Reitbrook 24.06.16_2.0	2.64	2.522	0.118
Reitbrook 25.01.16_1.0	1.29	1.319	-0.0288

Reitbrook 25.01.16_2.0	1.29	1.406	-0.116
Reitbrook 25.01.16_3.0	1.29	1.477	-0.187
Reitbrook 26.02.16_1.0	1.48	1.559	-0.0793
Reitbrook 26.02.16_2.0	1.48	1.437	0.0427
Reitbrook 26.02.16_3.0	1.48	1.251	0.229
Reitbrook 29.01.16_1.0	1.45	1.37	0.0798
Reitbrook 29.01.16_2.0	1.45	1.284	0.166
Reitbrook 29.01.16_3.0	1.45	1.394	0.0564
Reitbrook 08.07.16_1.0	2.8	2.798	0.00158
Reitbrook 08.07.16_2.1	2.8	2.838	-0.0383
Reitbrook 08.07.16_3.0	2.8	2.805	-0.00543
Reitbrook 11.07.16_1.0	2.92	2.826	0.0938
Reitbrook 11.07.16_2.1	2.92	2.821	0.0987
Reitbrook 11.07.16_3.0	2.92	2.906	0.0141
Reitbrook 28.06.16_1.0	2.7	2.817	-0.117
Reitbrook 28.06.16_2.0	2.7	2.711	-0.011
Reitbrook 28.06.16_3.0	2.7	2.69	0.00957
Reitbrook 30.06.16_1.0	3	2.833	0.167
Reitbrook 30.06.16_2.0	3	2.939	0.0611
Reitbrook 30.06.16_3.0	3	2.831	0.169

Table C. 2: oDM – Single Calibration Model Report (Min-max Normalisation).

Sample Name	Referans Value	Estimated Value by NIR	Difference
Reitbrook_25.01.16_1.0	70.63	70.7	-0.067
Reitbrook_25.01.16_2.0	70.63	70.35	0.28
Reitbrook_25.01.16_3.0	70.63	70.87	-0,243
Reitbrook_29.01.16_1.0	71.05	70.92	0.132
Reitbrook_29.01.16_2.0	71.05	71.83	0.779
Reitbrook_29.01.16_3.0	71.05	71.31	-0.259
Reitbrook_05.02.16_1.0	70.007	69.52	0.487
Reitbrook_05.02.16_2.0	70.007	70.3	-0.292
Reitbrook_05.02.16_3.0	70.007	70.4	-0.292
Reitbrook_16.02.16_1.0	71.424	70.94	0.481
Reitbrook_26.02.16_1.0	70.453	71.18	-0.723
Reitbrook_26.02.16_2.0	70.453	69.92	0.53
Reitbrook_26.02.16_3.0	70.453	70.16	0.291
Reitbrook_11.03.16_1.0	71.037	72.02	-0.981
Reitbrook_11.03.16_2.0	71.037	71.89	-0.853
Reitbrook_11.03.16_3.0	71.037	71.78	-0.747
Reitbrook_18.03.16_1.0	71.65	71.72	-0.0706
Reitbrook_18.03.16_2.0	71.65	72.43	-0.784
Reitbrook_18.03.16_3.0	71.65	72.71	-1.06
Reitbrook_06.04.16_2.0	72.169	72.74	-0.576
Reitbrook_06.04.16_2.1	72.169	70.85	1.32
Reitbrook_06.04.16_3.0	72.169	72.83	-0.661
Reitbrook_06.04.16_3.1	72.169	71.02	1.15
Reitbrook_06.05.16_2.0	72.487	73.35	-0.865
Reitbrook_06.05.16_3.0	72.487	73.8	-1.32
Reitbrook_12.05.16_1.0	72.053	72.47	-0.416
Reitbrook_12.05.16_2.0	72.053	72.7	-0.643
Reitbrook_12.05.16_3.0	72.053	72.9	-0.845
Reitbrook_21.04.16_1.0	72.065	72.24	-0.175
Reitbrook_21.04.16_2.0	72.065	71.04	1.02
Reitbrook_21.04.16_3.0	72.065	71.8	0.26
Reitbrook_20.05.16_1.0	72.781	72.83	-0.0535
Reitbrook_20.05.16_2.0	72.781	72.87	-0.0858
Reitbrook_20.05.16_3.0	72.781	73.53	-0.752
Reitbrook_03.06.16_1.0	74.7	74.42	0.276
Reitbrook_03.06.16_2.0	74.7	73.29	1.41
Reitbrook_03.06.16_3.0	74.7	73.75	0.948
Reitbrook_10.06.16_1.0	74.273	73.62	0.654
Reitbrook_10.06.16_2.0	74.273	74.14	0.135
Reitbrook_10.06.16_3.0	74.273	74.11	0.159
Reitbrook_15.06.16_1.0	78.56	79.66	-1.1
Reitbrook_15.06.16_2.0	78.56	78.03	0.531

Reitbrook_15.06.16_3.0	78.56	76.65	1.91
Reitbrook_17.06.16_1.0	74.63	75.37	-0.739
Reitbrook_17.06.16_2.0	74.63	75.94	-1.31
Reitbrook_21.06.16_1.0	75.64	76.33	-0.693
Reitbrook_21.06.16_2.0	75.64	75.76	-0.122
Reitbrook_21.06.16_3.0	75.64	75.52	0.118
Reitbrook_24.06.16_1.0	77.05	75.11	1.94
Reitbrook_24.06.16_2.0	77.05	75.4	1.65

Table C. 3: TNCD – Single Calibration Model Report (Substraction of Constant Offsets).

Sample Name	Referans Value	Estimated Value by NIR	Difference
Reitbrook_25.01.16_1.0	4.27	4.74	-0.47
Reitbrook_25.01.16_2.0	4.27	3.905	0.365
Reitbrook_25.01.16_3.0	4.27	4.436	-0.166
Reitbrook_29.01.16_1.0	4.76	4.842	-0.082
Reitbrook_29.01.16_2.0	4.76	4.789	-0.0287
Reitbrook_29.01.16_3.0	4.76	4.748	0.0118
Reitbrook_05.02.16_1.0	4.92	4.59	0.33
Reitbrook_05.02.16_2.0	4.92	4.908	0.0121
Reitbrook_05.02.16_3.0	4.92	5.017	-0.097
Reitbrook_26.02.16_1.0	5.54	5.479	0.0605
Reitbrook_26.02.16_2.0	5.54	5.086	0.454
Reitbrook_11.03.16_1.0	4.95	5.387	-0.437
Reitbrook_11.03.16_2.0	4.95	5.058	-0.108
Reitbrook_11.03.16_3.0	4.95	5.058	-0.247
Reitbrook_18.03.16_1.0	4.91	5.144	-0.234
Reitbrook_18.03.16_2.0	4.91	4.843	0.0667
Reitbrook_18.03.16_3.0	4.91	4.986	-0.0762
Reitbrook_06.04.16_2.0	5	5.12	-0.12
Reitbrook_06.04.16_2.1	5	5.265	-0.265
Reitbrook_06.04.16_3.0	5	5.099	-0.0991
Reitbrook_06.04.16_3.1	5	5.272	-0.272
Reitbrook_06.05.16_2.0	5.21	5.213	-0.00286
Reitbrook_06.05.16_3.0	5.21	5.278	-0.0675
Reitbrook_12.05.16_1.0	5.75	5.524	0.226
Reitbrook_12.05.16_2.0	5.75	5.507	0.243
Reitbrook_12.05.16_3.0	5.75	5.507	0.243
Reitbrook_21.04.16_1.0	5.13	5.05	0.0804
Reitbrook_21.04.16_2.0	5.13	5.022	0.108
Reitbrook_03.06.16_1.0	5.45	5.894	-0.444
Reitbrook_03.06.16_2.0	5.45	5.622	-0.172
Reitbrook_03.06.16_3.0	5.45	5.496	-0.0461
Reitbrook_10.06.16_1.0	5.78	5.568	0.212
Reitbrook_10.06.16_2.0	5.78	5.58	0.2
Reitbrook_10.06.16_3.0	5.78	5.497	0.283
Reitbrook_15.06.16_2.0	6.08	6.571	-0.491
Reitbrook_15.06.16_3.0	6.08	6.199	-0.119
Reitbrook_17.06.16_1.0	5.61	5.65	-0.0396
Reitbrook_17.06.16_2.0	5.61	5.638	-0.0282
Reitbrook_17.06.16_3.0	5.61	5.83	-0.22
Reitbrook_21.06.16_1.0	6.05	6.181	-0.131
Reitbrook_21.06.16_2.0	6.05	6.109	-0.0592
Reitbrook_21.06.16_3.0	6.05	6.088	-0.0382
Reitbrook_24.06.16_1.0	5.89	5.645	0.245

Reitbrook_24.06.16_2.0	5.89	5.614	0.276
Reitbrook_30.06.16_1.0	6.85	6.425	0.425
Reitbrook_30.06.16_2.0	6.85	6.641	0.209
Reitbrook_08.07.16_1.0	6.41	6.273	0.137
Reitbrook_08.07.16_2.0	6.41	6.472	-0.0621
Reitbrook_08.07.16_3.0	6.41	6.265	0.145
Reitbrook_11.07.16_1.0	5.84	5.904	-0.0639
Reitbrook_11.07.16_2.0	5.84	5.982	-0.142
Reitbrook_11.07.16_3.0	5.84	6.114	-0.274

Table C. 4: VFA – Single Calibration Model Report (Min-max Normalisation).

Sample Name	Referans Value	Estimated Value by NIR	Difference
Reitbrook_03.06.16_1.0	490	1508	-1020
Reitbrook _03.06.16_2.0	490	-688.2	1180
Reitbrook _03.06.16_3.0	490	-37.86	528
Reitbrook _05.02.16_1.0	1182	-1307	2490
Reitbrook _05.02.16_2.0	1182	82.99	1100
Reitbrook _05.02.16_3.0	1182	26.89	1160
Reitbrook _06.04.16_2.0	570	2641	-2070
Reitbrook _06.04.16_2.1	570	747.7	-178
Reitbrook _06.04.16_3.0	570	3510	-2940
Reitbrook _06.04.16_3.1	570	1252	-682
Reitbrook _06.05.16_1.0	439	3837	-3400
Reitbrook _06.05.16_2.0	439	1273	-834
Reitbrook _06.05.16_3.0	439	2157	-1720
Reitbrook _10.06.16_1.0	3264	3516	-252
Reitbrook _10.06.16_2.0	3264	4682	-1420
Reitbrook _10.06.16_3.0	3264	3739	-475
Reitbrook _11.03.16_1.0	73	2237	-2160
Reitbrook _11.03.16_2.0	73	1231	-1160
Reitbrook _11.03.16_3.0	73	906.7	-834
Reitbrook _12.05.16_1.0	840	1884	-1040
Reitbrook _12.05.16_2.0	840	1638	-798
Reitbrook _12.05.16_3.0	840	1926	-1090
Reitbrook _15.06.16_2.0	5100	9187	-4090
Reitbrook _15.06.16_3.0	5100	8324	-3220
Reitbrook _16.02.16_1.0	412	322.8	89.2
Reitbrook _17.06.16_1.0	8318	8728	-410
Reitbrook _17.06.16_2.0	8318	9659	-1340
Reitbrook _17.06.16_3.0	8318	11570	-3250
Reitbrook _18.03.16_1.0	491	566	-75
Reitbrook _18.03.16_2.0	491	1748	-1260
Reitbrook _18.03.16_3.0	491	751.4	-260
Reitbrook _20.05.16_1.0	792	2265	-1470
Reitbrook _20.05.16_2.0	792	1132	-340
Reitbrook _20.05.16_3.0	792	2971	-2180
Reitbrook _21.04.16_1.0	934	3777	-2840
Reitbrook _21.04.16_2.0	934	1222	-288
Reitbrook _21.04.16_3.0	934	786.4	148
Reitbrook _21.06.16_1.0	8849	7937	912
Reitbrook _21.06.16_2.0	8849	6768	2080
Reitbrook _21.06.16_3.0	8849	5452	3400
Reitbrook _24.06.16_1.0	10997	9442	1550
Reitbrook _24.06.16_2.0	10997	9087	1910
Reitbrook _25.01.16_1.0	812	1507	-695
Reitbrook _25.01.16_2.0	812	2711	-1900

Reitbrook _25.01.16_3.0	812	2883	-2070
Reitbrook _26.02.16_1.0	192	-149.1	341
Reitbrook _26.02.16_2.0	192	-990.3	1180
Reitbrook _26.02.16_3.0	192	-2787	2980
Reitbrook _29.01.16_1.0	1201	-1795	3000
Reitbrook _29.01.16_2.0	1201	-1506	2710
Reitbrook _29.01.16_3.0	1201	-2629	3830
Reitbrook _08.07.16_1.0	13566	10740	2830
Reitbrook _08.07.16_2.1	13566	12090	1480
Reitbrook _08.07.16_3.0	13566	10970	2590
Reitbrook _11.07.16_1.0	13014	11090	1920
Reitbrook _11.07.16_2.1	13014	10500	2510
Reitbrook _11.07.16_3.0	13014	12080	934
Reitbrook _28.06.16_1.0	12854	13920	-1060
Reitbrook _28.06.16_2.0	12854	12250	603
Reitbrook _28.06.16_3.0	12854	11780	1070
Reitbrook _30.06.16_1.0	13865	13710	156
Reitbrook _30.06.16_2.0	13865	14320	-458

Table C. 5: NH_4-N – Single Calibration Model Report (Multiplicative Scatter).

Sample Name	Referans Value	Estimated Value by NIR	Difference
Reitbrook_25.01.16_1.0	3158	3293	-135
Reitbrook_25.01.16_2.0	3158	3202	-44.3
Reitbrook_25.01.16_3.0	3158	3312	-154
Reitbrook_29.01.16_1.0	3459	3412	46.8
Reitbrook_29.01.16_2.0	3459	3433	26,2
Reitbrook_29.01.16_3.0	3459	3397	62.1
Reitbrook_16.02.16_1.0	3435	3501	-65,7
Reitbrook_26.02.16_1.0	3910	3637	273
Reitbrook_11.03.16_1.0	3624	3537	87.3
Reitbrook_11.03.16_2.0	3624	3454	170
Reitbrook_11.03.16_3.0	3624	3494	130
Reitbrook_18.03.16_1.0	3361	3444	-83,4
Reitbrook_18.03.16_2.0	3361	3469	-108
Reitbrook_18.03.16_3.0	3361	3493	-132
Reitbrook_06.04.16_1.0	3330	3372	-42.3
Reitbrook_06.04.16_2.0	3330	3392	-61.8
Reitbrook_06.04.16_2.1	3330	3504	-174
Reitbrook_06.04.16_3.0	3330	3390	-59.9
Reitbrook_06.04.16_3.1	3330	3452	-122
Reitbrook_06.05.16_1.0	4168	3909	259
Reitbrook_12.05.16_1.0	3644	3792	-148
Reitbrook_12.05.16_2.0	3644	3776	-132
Reitbrook_12.05.16_3.0	3644	3819	-175
Reitbrook_20.05.16_1.0	3929	3993	-63.9
Reitbrook_20.05.16_2.0	3929	3908	21.4
Reitbrook_20.05.16_3.0	3929	4010	-81.3
Reitbrook_03.06.16_1.0	3929	3837	92.4
Reitbrook_03.06.16_2.0	3929	3837	102
Reitbrook_03.06.16_3.0	3929	3834	95.1
Reitbrook_30.06.16_1.0	4009	3838	171
Reitbrook_30.06.16_2.0	4009	4026	-16.9
Reitbrook_30.06.16_3.0	4009	3874	135
Reitbrook_10.06.16_1.0	3770	3770	-0.196
Reitbrook_10.06.16_2.0	3770	3787	-17.1
Reitbrook_10.06.16_3.0	3770	3808	-37.8
Reitbrook_15.06.16_2.0	4196	4307	-111
Reitbrook_15.06.16_3.0	4196	4128	67.7
Reitbrook_17.06.16_1.0	4147	3866	281
Reitbrook_17.06.16_2.0	4147	4051	96.1
Reitbrook_21.06.16_1.0	3941	3990	-49.1
Reitbrook_21.06.16_2.0	3941	4066	-125
Reitbrook_21.06.16_3.0	3941	4055	-114
Reitbrook_28.06.16_1.0	3891	4157	-266
Reitbrook_28.06.16_2.0	3891	3910	-18.8

Reitbrook_28.06.16_3.0	3891	3774	117
Reitbrook_08.07.16_1.0	3945	3876	69.5
Reitbrook_08.07.16_2.0	3945	3931	13.9
Reitbrook_08.07.16_3.0	3945	3867	77.5
Reitbrook_08.07.16_1.0	3895	3849	46.2
Reitbrook_08.07.16_2.0	3895	3900	-4.77
Reitbrook_08.07.16_3.0	3895	4008	-113

Table C. 6: HCO_3^- – Single Calibration Model Report (Min-max Normalisation).

Sample	Referans Value	Estimated Value by NIR	Difference
Reitbrook_25.01.16_2.0	14986	14340	647
Reitbrook_25.01.16_3.0	14986	15420	-431
Reitbrook_05.02.16_1.0	15230	16420	-1190
Reitbrook_05.02.16_2.0	15230	16920	-1690
Reitbrook_05.02.16_3.0	15230	15830	-599
Reitbrook_16.02.16_1.0	15938	17090	-1160
Reitbrook_26.02.16_1.0	16353	16560	-204
Reitbrook_26.02.16_2.0	16353	16650	-301
Reitbrook_11.03.16_1.0	17426	17070	360
Reitbrook_11.03.16_2.0	17426	17070	360
Reitbrook_11.03.16_2.0	17426	18080	-659
Reitbrook_11.03.16_3.0	17426	18310	-882
Reitbrook_18.03.16_1.0	16621	16870	-251
Reitbrook_06.04.16_2.1	17280	17070	207
Reitbrook_06.04.16_2.0	17280	17210	66.5
Reitbrook_06.04.16_3.0	17280	17630	-352
Reitbrook_06.04.16_3.1	17280	17120	164
Reitbrook_21.04.16_1.0	18183	17490	689
Reitbrook_21.04.16_2.0	18183	17100	1080
Reitbrook_21.04.16_3.0	18183	18170	8,28
Reitbrook_06.05.16_1.0	19208	18610	598
Reitbrook_06.05.16_2.0	19208	19060	152
Reitbrook_06.05.16_3.0	19208	19120	84.7
Reitbrook_12.05.16_1.0	19037	17980	1060
Reitbrook_12.05.16_2.0	19037	18730	310
Reitbrook_12.05.16_3.0	19037	18250	787
Reitbrook_20.05.16_1.0	19476	17820	1660
Reitbrook_20.05.16_2.0	19476	18430	1040
Reitbrook_20.05.16_3.0	19476	18170	1300
Reitbrook_03.06.16_1.0	20550	19360	1190
Reitbrook_03.06.16_2.0	20550	19620	929
Reitbrook_03.06.16_3.0	20550	20530	24,40
Reitbrook_10.06.16_1.0	16304	17790	1490,00
Reitbrook_10.06.16_2.0	16304	17750	1450,00
Reitbrook_15.06.16_1.0	16596	15830	765
Reitbrook_15.06.16_2.0	16596	17050	-452
Reitbrook_15.06.16_3.0	16596	16920	-322
Reitbrook_17.06.16_1.0	16743	15700	1040
Reitbrook_17.06.16_2.0	16743	16280	463
Reitbrook_17.06.16_3.0	16743	17150	-403
Reitbrook_21.06.16_1.0	16010	17090	-1080
Reitbrook_21.06.16_2.0	16010	17340	-1330
Reitbrook_21.06.16_3.0	16010	17010	-999

Table C. 7: DM – Multi Calibration Model Report (Multiplicative Scatter).

Sample Name	Referans Value	Estimated Value by NIR	Difference
Reitbrook_03.06.16_1.0	2.15	2.61	-0.46
Reitbrook _03.06.16_2.0	2.15	2.611	-0.461
Reitbrook _03.06.16_3.0	2.15	3.461	-1.31
Reitbrook _05.02.16_1.0	1.34	2.313	-0.973
Reitbrook _05.02.16_2.0	1.34	1.435	-0.0947
Reitbrook _05.02.16_3.0	1.34	1.742	-0.402
Reitbrook _06.04.16_1.0	1.69	1.399	0.291
Reitbrook _06.04.16_2.0	1.69	1.726	-0.0357
Reitbrook _06.04.16_2.1	1.69	1.116	0.574
Reitbrook _06.04.16_3.0	1.69	2.118	-0.428
Reitbrook _06.04.16_3.1	1.69	0.8233	0.867
Reitbrook _06.05.16_1.0	2.01	3.292	-1.28
Reitbrook _06.05.16_2.0	2.01	2.88	-0.87
Reitbrook _06.05.16_3.0	2.01	2.942	-0.932
Reitbrook _10.06.16_1.0	2.22	2.413	-0.193
Reitbrook _10.06.16_2.0	2.22	1.966	0.254
Reitbrook _10.06.16_3.0	2.22	2.372	-0.152
Reitbrook _11.03.16_1.0	1.57	1.538	0.0322
Reitbrook _11.03.16_2.0	1.57	1.484	0.0859
Reitbrook_ 11.03.16_3.0	1.57	1.42	0.15
Reitbrook _12.05.16_1.0	1.92	1.721	0.199
Reitbrook _12.05.16_2.0	1.92	1.369	0.551
Reitbrook _12.05.16_3.0	1.92	1.867	0.0528
Reitbrook _15.06.16_1.0	2.69	3.3	-0.61
Reitbrook _15.06.16_2.0	2.69	3.164	-0.474
Reitbrook _15.06.16_3.0	2.69	3.356	-0.666
Reitbrook _16.02.16_1.0	1.43	0.8413	0.589
Reitbrook _17.06.16_1.0	2.53	2.264	0.266
Reitbrook _17.06.16_2.0	2.53	2.233	0.297
Reitbrook _17.06.16_3.0	2.53	2.735	-0.205
Reitbrook _18.03.16_1.0	1.56	1.974	-0.414
Reitbrook _18.03.16_2.0	1.56	2.944	-1.38
Reitbrook _18.03.16_3.0	1.56	2.675	-1.12
Reitbrook _20.05.16_1.0	2	2.015	-0.0152
Reitbrook _20.05.16_2.0	2	1.747	0.253
Reitbrook _20.05.16_3.0	2	2.224	-0.224
Reitbrook _21.04.16_1.0	1.95	2.036	-0.0858
Reitbrook _21.04.16_2.0	1.95	2.015	-0.0648
Reitbrook _21.04.16_3.0	1.95	2.444	-0.494
Reitbrook _21.06.16_1.0	2.39	2.894	-0.504
Reitbrook _21.06.16_2.0	2.39	2.408	-0.0183
Reitbrook _21.06.16_3.0	2.39	3.14	-0.75
Reitbrook _24.06.16_1.0	2.64	2.141	0.499
Reitbrook _24.06.16_2.0	2.64	2.203	0.437

Reitbrook _25.01.16_1.0	1.29	0.6997	0.59
Reitbrook _25.01.16_2.0	1.29	0.3728	0.917
Reitbrook _25.01.16_3.0	1.29	1.538	-0.248
Reitbrook _26.02.16_1.0	1.48	0.7414	0.739
Reitbrook_ 26.02.16_2.0	1.48	1.713	-0.233
Reitbrook _26.02.16_3.0	1.48	1.552	-0.0715
Reitbrook _29.01.16_1.0	1.45	1.597	-0.147
Reitbrook _29.01.16_2.0	1.45	2.263	-0.813
Reitbrook _29.01.16_3.0	1.45	2.314	-0.864
Fermenter1_1m_0_01.09.15_1.0	5.65	5.286	0.364
Fermenter1_1m_0_01.09.15_2.0	5.65	5.012	0.638
Fermenter1_1m_0_01.09.15_3.0	5.65	5.653	-0.00255
Fermenter1_1m_90_27.08.15_1.0	5.65	5.577	0.0729
Fermenter1_1m_90_27.08.15_2.0	4.98	5.488	-0.508
Fermenter1_1m_90_27.08.15_3.0	4.98	5.62	-0.64
Fermenter1_1m_180_27.08.15_1.0	4.98	6.196	-1.22
Fermenter1_1m_180_27.08.15_2.0	6.83	6.07	0.76
Fermenter1_1m_180_27.08.15_3.0	6.83	6.022	0.808
Fermenter1_1_02.04.15	6.83	5.659	1.17
Fermenter1_1_28.05.15	5.22	6.64	-1.42
Fermenter1_2_02.04.15	5.22	6.478	-1.26
Fermenter1_2_28.05.15	5.22	6.902	-1.68
Fermenter1_3m_0_01.09.15_1.0	7.75	6.506	1.24
Fermenter1_3m_0_01.09.15_2.0	7.75	6.371	1.38
Fermenter1_3m_0_01.09.15_2.1	7.75	7.219	0.531
Fermenter1_3m_0_01.09.15_3.0	7.77	6.175	1.6
Fermenter1_3m_0_01.09.15_3.1	7.77	7.115	0.655
Fermenter1_3m_90_01.09.15_1!.0	7.77	6.168	1.6
Fermenter1_3m_90_01.09.15_2.0	6.32	6.359	-0.0387
Fermenter1_3m_90_01.09.15_3.0	6.32	6.314	0.00625
Fermenter1_3m_180_01.09.15_1.0	6.32	6.014	0.306
Fermenter1_3m_180_01.09.15_2.0	5.38	5.897	-0.517
Fermenter1_3m_180_01.09.15_3.0	5.38	6.156	-0.776
Fermenter1_3m_270_01.09.15_1.0	5.38	6.369	-0.989
Fermenter1_3m_270_01.09.15_2.0	5.81	6.667	-0.857
Fermenter1_3m_270_01.09.15_3.0	5.81	6.14	-0.33
Fermenter1_3_02.04.15	5.81	6.484	-0.674
Fermenter1_3_28.05.15	5.96	6.522	-0.562
Fermenter1_inside_01.09.15_1.0	5.96	6.239	-0.279
Fermenter1_inside_01.09.15_2.0	5.96	6.318	-0.358
Fermenter1_inside_01.09.15_3.0	5.67	6.046	-0.376
Fermenter1_inside_1.0	5.67	6.685	-1.02
Fermenter1_inside_2.0	5.67	5.756	-0.0857
Fermenter1_inside_3.0	4.91	6.581	-1.67
Fermenter2_1_28.05.15	6.55	7.328	-0.778
Fermenter2_2_02.04.15	6.55	7.62	-1.07
Fermenter2_2_28.05.15	6.55	7.328	-0.778
Fermenter2_3m_1.0	8.59	7.3	1.29
Fermenter2_3m_26.06.15_2.0	8.59	7.873	0.717

Fermenter2_3m_26.06.15_3.0	8.21	8.407	-0.197
Fermenter2_3_02.04.15	8.21	7.619	0.591
Fermenter2_3_28.05.15	8.21	6.762	1.45
Fermenter2_inside_2.0	8.15	6.498	1.65
Fermenter2_inside_3.0	8.15	6.432	1.72
Fermenter2_inside_3.1	6.25	6.636	-0.386
Reitbrook _08.07.16_1.0	2.8	2.46	0.34
Reitbrook _08.07.16_2.1	2.8	2.501	0.299
Reitbrook _08.07.16_3.0	2.8	2.492	0.308
Reitbrook _11.07.16_1.0	2.9243	2.711	0.213
Reitbrook_ 11.07.16_2.1	2.9243	2.517	0.408
Reitbrook _11.07.16_3.0	2.9243	2.721	0.204
Reitbrook _28.06.16_1.0	2.7	2.487	0.213
Reitbrook _28.06.16_2.0	2.7	2.613	0.0866
Reitbrook _28.06.16_3.0	2.7	2.43	0.27
Reitbrook _30.06.16_1.0	3	2.201	0.799
Reitbrook _30.06.16_2.0	3	2.412	0.588
Reitbrook _30.06.16_3.0	3	2.373	0.627

Table C. 8: oDM – Multi Calibration Model Report (Without Pretreatment).

Sample	Referans Value	Estimated Value by NIR	Difference
Reitbrook_03.06.16_1.0	74.7	73.65	1.05
Reitbrook _03.06.16_2.0	74.7	73.03	1.67
Reitbrook _03.06.16_3.0	74.7	73.32	1.38
Reitbrook _05.02.16_1.0	70.007	69.27	0.741
Reitbrook _05.02.16_2.0	70.007	69.69	0.313
Reitbrook _05.02.16_3.0	70.007	69.84	0.165
Reitbrook _06.04.16_1.0	72.169	74.64	-2.47
Reitbrook _06.04.16_2.0	72.169	72.88	-0.711
Reitbrook _06.04.16_2.1	72.169	71.24	0.931
Reitbrook _06.04.16_3.0	72.169	72.81	-0.641
Reitbrook _06.04.16_3.1	72.169	71.53	0.643
Reitbrook _06.05.16_1.0	72.487	75.06	-2.57
Reitbrook _06.05.16_2.0	72.487	73.77	-1.28
Reitbrook _06.05.16_3.0	72.487	73.8	-1.31
Reitbrook _10.06.16_1.0	74.273	73.41	0.864
Reitbrook _10.06.16_2.0	74.273	74.27	-0.00145
Reitbrook _10.06.16_3.0	74.273	74.43	-0.152
Reitbrook _11.03.16_1.0	71.037	71.95	-0.912
Reitbrook _11.03.16_2.0	71.037	72.23	-1.19
Reitbrook _11.03.16_3.0	71.037	72.3	-1.26
Reitbrook _12.05.16_1.0	72.053	72.23	-0.173
Reitbrook _12.05.16_2.0	72.053	72.93	-0.873
Reitbrook _12.05.16_3.0	72.053	73	-0.947
Reitbrook _15.06.16_1.0	78.56	77.66	0.899
Reitbrook _15.06.16_2.0	78.56	76.41	2.15
Reitbrook _15.06.16_3.0	78.56	75.6	2.96
Reitbrook _16.02.16_1.0	71.424	71.08	0.341
Reitbrook _17.06.16_1.0	74.63	75.38	-0.753
Reitbrook _17.06.16_2.0	74.63	75.8	-1.17
Reitbrook _17.06.16_3.0	74.63	76.76	-2.13
Reitbrook _18.03.16_1.0	71.65	72.51	-0.859
Reitbrook _18.03.16_2.0	71.65	72.83	-1.18
Reitbrook _18.03.16_3.0	71.65	73.42	-1.77
Reitbrook _20.05.16_1.0	72.781	72.13	0.655
Reitbrook _20.05.16_2.0	72.781	72.36	0.426
Reitbrook _20.05.16_3.0	72.781	72.62	0.162
Reitbrook _21.04.16_1.0	72.065	73.23	-1.16
Reitbrook _21.04.16_2.0	72.065	72.31	-0.245
Reitbrook _21.04.16_3.0	72.065	73.32	-1.26
Reitbrook _21.06.16_1.0	75.64	75.09	0.549
Reitbrok _21.06.16_2.0	75.64	7.94	0.7
Reitbrook _21.06.16_3.0	75.64	74.67	0.969
Reitbrook _24.06.16_1.0	77.05	75.55	1.5
Reitbrook _24.06.16_2.0	77.05	75.92	1.13

Reitbrook _25.01.16_1.0	70.63	70.27	0.362
Reitbrook _25.01.16_2.0	70.63	70.28	0.351
Reitbrook _25.01.16_3.0	70.63	70.3	0.329
Reitbrook _26.02.16_1.0	70.453	70.95	-0.502
Reitbrook_ 26.02.16_2.0	70.453	70.27	0.181
Reitbrook _26.02.16_3.0	70.453	70.05	0.404
Reitbrook _29.01.16_1.0	71.05	71.23	-0.177
Reitbrook _29.01.16_2.0	71.05	71.05	0.00477
Reitbrook_ 29.01.16_3.0	71.05	71.59	-0.542
Fermenter1_1m_180_27.08.15_2.0	75.18	77.58	-2.4
Fermenter1_1m_180_27.08.15_3.0	75.18	78.02	-2.84
Fermenter1_1_02.04.15	75.18	77.47	-2.29
Fermenter1_1_28.05.15	78.07	77.56	0.51
Fermenter1_2_02.04.15	78.07	76.79	1.28
Fermenter1_2_28.05.15	78.07	78.76	-0.69
Fermenter1_3m_0_01.09.15_1.0	78.07	77.64	0.431
Fermenter1_3m_0_01.09.15_2.0	78.07	77.18	0.89
Fermenter1_3m_0_01.09.15_2.1	78.07	76.81	1.26
Fermenter1_3m_0_01.09.15_3.0	78.03	77.77	0.263
Fermenter1_3m_0_01.09.15_3.1	78.03	77.07	0.96
Fermenter1_3m_90_01.09.15_1!.0	78.03	77.29	0.739
Fermenter1_3m_90_01.09.15_2.0	78.6	76.98	1.62
Fermenter1_3m_90_01.09.15_3.0	78.6	77.4	1.2
Fermenter1_3m_180_01.09.15_1.0	78.6	77.2	1.4
Fermenter1_3m_180_01.09.15_2.0	75.44	77.67	-2.23
Fermenter1_3m_180_01.09.15_3.0	75.44	77.19	-1.75
Fermenter1_3m_270_01.09.15_1.0	75.44	77.25	-1.81
Fermenter1_3m_270_01.09.15_2.0	78.81	76.75	2.06
Fermenter1_3m_270_01.09.15_3.0	78.81	76.64	2.17
Fermenter1_3_02.04.15	78.81	76.27	2.54
Fermenter1_3_28.05.15	78.86	76.88	1.98
Fermenter1_inside_01.09.15_1.0	78.86	78.13	0.734
Fermenter1_inside_01.09.15_2.0	78.86	78.16	0.699
Fermenter1_inside_01.09.15_3.0	78.57	77.55	1.02
Fermenter1_inside_1.0	78.57	79.06	-0.493
Fermenter1_inside_2.0	78.57	79.87	-1.3
Fermenter1_inside_3.0	76.25	78.46	-2.21
Fermenter2'_1_02.04.15	76.25	75.28	0.966
Fermenter2_1_02.04.15	76.25	74.76	1.49
Fermenter2_3m_26.06.15_1.0	74.12	75.44	-1.32
Fermenter2_3m_26.06.15_2.0	74.12	75.55	-1.43
Fermenter2_3m_26.06.15_3.0	76.5	74.59	1.91
Fermenter2_inside_1.0	76.81	77.4	-0.585
Fermenter2_inside_2.0	76.81	77.16	-0.346
Fermenter2_inside_3.0	76.81	77.91	-1.1
Fermenter2_inside_3.1	77.92	77.86	0.0598
Reitbrook_ 28.06.16_1.0	77.31	77.95	-0.64
Reitbrook _28.06.16_2.0	77.31	76.97	0.345
Reitbrook _28.06.16_3.0	77.31	76.34	0.972

Table C. 9: HCO_3^- – Multi Calibration Model Report (Multiplicative Scatter).

Sample	Referans Value	Estimated Value by NIR	Difference
Reitbrook _05.02.16_1.0	15230	15470	-240
Reitbrook _05.02.16_2.0	15230	15310	-75.8
Reitbrook _05.02.16_3.0	15230	16440	-1210
Reitbrook _06.04.16_1.0	17280	17670	-386
Reitbrook _06.04.16_2.0	17280	17050	227
Reitbrook _06.04.16_3.0	17280	17100	181
Reitbrook _06.04.16_3.1	17280	16340	941
Reitbrook _10.06.16_1.0	16304	16270	30.7
Reitbrook _10.06.16_2.0	16304	16500	-193
Reitbrook _10.06.16_3.0	16304	16790	-487
Reitbrook _11.03.16_1.0	17426	16570	854
Reitbrook _11.03.16_2.0	17426	16560	862
Reitbrook _11.03.16_3.0	17426	17120	301
Reitbrook _15.06.16_2.0	16596	15740	857
Reitbrook_ 15.06.16_3.0	16596	15970	626
Reitbrook _16.02.16_1.0	15938	15570	369
Reitbrook _17.06.16_1.0	16743	16690	49.5
Reitbrook _17.06.16_2.0	16743	17000	-257
Reitbrook _17.06.16_3.0	16743	17490	-744
Reitbrook _18.03.16_1.0	16621	17160	-536
Reitbrook_ 18.03.16_2.0	16621	17270	-648
Reitbrook _18.03.16_3.0	16621	17630	-1010
Reitbrook _21.04.16_1.0	18183	17240	938
Reitbrook _21.04.16_2.0	18183	17290	894
Reitbrook _21.04.16_3.0	18183	17460	720
Reitbrook _21.06.16_1.0	16010	16310	-299
Reitbrook _21.06.16_2.0	16010	16210	-199
Reitbrook _21.06.16_3.0	16010	16330	-324
Reitbrook _25.01.16_1.0	14986	15890	-906
Reitbrook _25.01.16_2.0	14986	15730	-744
Reitbrook _25.01.16_3.0	14986	15530	-549
Reitbrook _26.02.16_1.0	16353	16350	0.78
Reitbrook _26.02.16_2.0	16353	16070	286
Reitbrook _26.02.16_3.0	16353	16450	-98.9
Fermenter1_1m_180_27.08.15_2.0	17426	18180	-754
Fermenter1_1m_180_27.08.15_3.0	17426	18250	-820
Fermenter1_1_02.04.15	17426	18260	-836
Fermenter1_1_28.05.15	18598	18760	-158
Fermenter1_2_02.04.15	18598	18170	430
Fermenter1_2_28.05.15	18598	18680	-82.9
Fermenter1_3m_0_01.09.15_1.0	18890	18450	436
Fermenter1_3m_0_01.09.15_2.0	18890	18390	498
Fermenter1_3m_0_01.09.15_2.1	18890	18860	32.6
Fermenter1_3m_0_01.09.15_3.0	18793	18360	434

Fermenter1_3m_0_01.09.15_3.1	18793	18560	236
Fermenter1_3m_90_01.09.15_1!.0	18793	18200	588
Fermenter1_3m_90_01.09.15_2.0	18062	18310	-244
Fermenter1_3m_90_01.09.15_3.0	18062	18360	-297
Fermenter1_3m_180_01.09.15_1.0	18062	18210	-148
Fermenter1_3m_180_01.09.15_2.0	18208	18140	69.4
Fermenter1_3m_180_01.09.15_3.0	18208	18230	-25.5
Fermenter1_3m_270_01.09.15_1.0	18208	18270	-65.5
Fermenter1_3m_270_01.09.15_2.0	17768	18300	-535
Fermenter1_3m_270_01.09.15_3.0	17768	18240	-471
Fermenter1_3_02.04.15	17768	18150	-382
Fermenter1_3_28.05.15	18452	18380	67.3
Fermenter1_inside_01.09.15_1.0	18452	18050	404
Fermenter1_inside_01.09.15_2.0	18452	18110	339
Fermenter1_inside_01.09.15_3.0	18500	17980	522
Fermenter1_inside_1.0	18500	18610	-108
Fermenter1_inside_2.0	18500	18130	375
Fermenter1_inside_3.0	18744	18290	452
Fermenter2'_1_02.04.15	18744	19190	-442
Fermenter2_3m_26.06.15_3.0	19525	19230	293
Fermenter2_3_02.04.15	19525	19150	371
Fermenter2_3_28.05.15	19525	18720	810

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