LIFE13/ENV/UK/000401 Project Quarterback

"Crude glycerine water used on-site as a feedstock in an anaerobic digestion reactor to produce the renewable fuel biogas"

Validation Report

Version: Final

Date: 31 July 2017

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Introduction

Project "Quarterback" is named after the intended delivery of a 25% reduction of CO2 emission of the Croda Gouda. Innovation comes mainly from conversion of glycerine containing water ex-hydrolysis to biogas in an anaerobic digestion process. The biogas is used as fuel for the production of fatty acids and partly replaces the natural gas demand.

The overall CO_2 emission reduction is not only reached by the production of biogas, but also by simultaneously avoiding the energy required for concentration of the glycerine water to crude glycerine prior to refining, and by a conversion of the existing Combined Heat and Power plant to a 10% higher efficiency.

Key to success of the project is the performance of the of the glycerine anaerobic digestion process. This specific technology is completely new for Croda but also new to industry in general. No other examples of industrial scale digestion of glycerine to biogas as a "mono" feedstock, i.e. without mixing with other organic and digestible feedstocks, are known. Also this digestion system is not an end-of pipe solution to convert waste into biogas but a regular processing step. Glycerine in itself is a marketable co-product from hydrolysis of fats and oils and as such can be refined into a marketable end-product.

To ensure an independent view on the performance of the system, validation of the digestion performance was contracted to the LeAF institute, providing independent and high quality advice on the development and implementation of sustainable environmental technologies for treatment and valorisation of organic residues and part of the Wageningen University, a.o. specialised in development of sustainable technologies.

Their report forms the main part of this validation report and is attached as Addendum A.

The project Quarterback primary objectives are (reference year: 2012)

- Reduction of the facility CO2 emissions by 25% (net 12.000 tonnes CO2/yr);
- Reduction of the facility electricity demand by 6% (2.400 MWh);
- Reduction of the chemical demand for process cleaning;
- Reduction of the water and chemical consumption for boiler feed water (20.000 ton/yr).

All data necessary for validation have been extracted from the Croda Gouda site process data collection system or were measured by analysis and subsequently reported on a daily, weekly, monthly or yearly basis. The table below shows the actual monitoring activities, which are used for operations but also for validation purposes.

Action C1. Monitoring impact of the project on environmental problem targeted

Environment indicator	When?	Where?	Who?	What?	How?
Process performance	Continuous	Process control and SCADA systems	Process operators	All key processing parameters: conversion degree [%], biogas composition [%], biogas flow [Mn3/h]	On-line measurements, ISO standard measurements
Process performance digestion and boiler	Daily	At various locations in the field	Process operators	Samples taken from process: pH, dry solids content [%], FOS/TAC, COD	Laboratory analysis, Croda IBS standard (ISO 9001)

Process parameters Effluent Treatment plant	Continuous and daily	ETP influent and effluent	Surface water authorities (RWS)	Samples taken from process: COD, dry solids [%]	Continuous and laboratory analysis, Croda IBS standard (ISO 9001)
Emissions and energy consumption	Monthly	Site utility/ financial report	Financial accountant	Monthly consumption of natural gas, biogas [GJ] electricity [MWh]	Meter readings, ISO standard measurements
Boiler efficiency	Monthly	Site utility/ financial report	Financial accountant	Energy output divided by energy input [%]	Calculation, Croda IBS standard (ISO 9001)
Digestion output	Monthly	Monthly subsidy reporting	Subsidy authorities (CertiQ/RVO)	Biogas generated, green power and heat [GJ]	Meter readings and monthly calculations/ reporting
Energy consumption, odour and noise complaints	Quarterly	Croda Group central reporting	Group SHE Manager	Quarterly consumption of natural gas, biogas, electricity [GJ]	Meter readings, ISO standard measurements
Emissions and energy consumption	Yearly	Croda Group Sustainability report	VP Sustainability	Non-fossil fuel consumption [GJ], GHG emission [tpa]	Based on quarterly site reporting, NEA standard
Emissions and energy consumption	Yearly	NL industrial energy reduction plan (MEE)	SHE manager	Yearly consumption of natural gas, biogas [GJ], electricity [MWh]	Meter readings. NEA standard
Emissions and energy consumption	Yearly	EU-ETS scheme via NL Emission authorities (NEA)	SHE manager	Yearly consumption of natural gas, biogas [GJ], electricity [MWh]	Meter readings NEA standard
Emissions	Yearly	Boiler and gas engine stack	External Certified Agency (Blauw Consultants)	NOx [tpa], flue gas composition [%]	Validation of emission, NEA standard

Data collection and results

All parameters of importance to the process of glycerine digestion and subsequent steps of biogas production, biogas treatment, combustion in the boiler and gas engine, sludge separation and treatment of effluent water streams are measured continuously via the Siemens DCS system. Effectively process parameters are measured on the following number of separate channels/locations:

Section 28.0 Boilerhouse	655
Section 31.0 Effluent Treatment Plant	1.621
Section 33.0 Glycerine Digestion	420

These measuring devices can be found on the P&I Diagrams ("Process & Instrumentation Diagrams") of which for the above three sections of the site there are in total 60 separate diagrams, covering the entire section.

Process operators monitor the process on a 24/7 basis and ensure proper performance by adjusting the variables when necessary. For the same purpose physical samples are taken at key locations in the process, e.g. of the feed stream and from the reactors, and analysed in the laboratory on site to check parameters that cannot be measured on-line such as glycerine and sludge composition.

The data from the DCS system are collected and stored in a SCADA system called "Aspen". This system collects data on a certain interval, usually a value is recorded and stored every 6 seconds. These are available for reporting and data analysis and are infinitely available as they are stored on hard drives.

All invoiced water and energy, i.e. natural gas and electrical power, is metered by calibrated and certified measuring devices as well as the meters related to verification of subsidies that are received. These metering data and the above Aspen data are used to compile monthly, quarterly and yearly reports in the Croda Gouda finance department, for central reporting to the Croda Group and for reporting to the NL Government.

For validation by Croda and by LeAF of the digestion techonology, mainly on-line data from the Aspen system have been used. A file is available as annex to the Final Report (Annex 6 Production data) showing all data per day of all parameters influencing the digestion performance. The key parameters are:

Glycerine water flow [average flow ton/h]

Crude biogas flow from reactors VS2000, VS3000 and VS4000 [average flow m3/h]

Combined biogas flow from reactors [corrected to Nm3/h]

Methane content in biogas [volume %]

Glycerine water flow from buffertank VS1000 to digestors [ton/h]

Biogas to gasengine [Nm3/h]

Biogas to boiler K10 [Nm3/h]

Glycerine water organic content COD [mg/l]

Calculated conversion efficiency [Mn3 CH4/kg COD]

Almost all measurement devices are certified and regularly calibrated to maintain accuracy.

For validation purposes from these data overall digestion performance is measured and calculated, with monthly results shown in the table below. From a technical and economical point of view the tabulated *conversion efficiency* is the most important variable as the organic part of the feed stream that is not converted to methane reduces benefits of the project and adds cost for further oxidation in the waste water treatment plant.

Month	Glycerine water [ton]	Biogas to utilities [mn3]	Biogas methane %	Conversion efficiency per day Mn3 CH4/kg COD
Tag number	415-00-FI0152.PV	280-SB-MB.Vb1tot	330-00-QI5310_1.PV	calc
Jun 2016	923	na	na	na
Jul 2016	863	40715	64.2	0.349
Aug 2016	2124	174050	58.7	0.346
Sep 2016	952	73339	50.3	0.331
Oct 2016	1728	153087	50.7	0.326
Nov 2016	3526	207610	58.4	0.310
Dec 2016	2178	191021	61.1	0.301
Jan 2017	3450	243974	60.1	0.286
Feb 2017	2706	231396	58.5	0.332
Mar 2017	3651	334307	57.8	0.340
Apr 2017	1745	131413	56.3	0.289
May 2017	2902	261649	58.1	0.341
Jun 2017	5099	430701	57.5	0.317
Total or average	**31848**	**2473262**	**57.64**	**0.323**

From the previously mentioned data file as presented with the Final Report (Annex 6 Production data) all other relevant digestion calculations can be done for detailed analysis, for instance as also shown in figure 15 in the Final Report, repeated below:

Operational parameters	Result	Unit
Glycerine water produced by hydrolysis	56.914	ton
Glycerine water digested	30.958	ton
Glycerine water fraction sent to digestion	54,4	%
Glycerine concentration, average	14,50	%
Average residence time in reactors (target 20-30)	66,9	days
COD digested @ 1,217 ton COD/ton glycerine	5.463*	ton

Biogas produced wet	3.340.643	M3
Biogas produced corrected by 0,865 (see Annex 5 Design data)	2.889.665	Nm3
CH_4 produced	1.658.668	Nm3
Biogas to engine plus boiler	2.496.675	Nm3
Biogas to flare	392.990	Nm3
Biogas effectively used	86,4	%
Electrical power generated from biogas	4.692	MWh
Heat generated from biogas	28.575	GJ
Final evaluation targets [Section B.5]		
Biogas yield: >90% [MPP 0,35 Nm3 CH_4/kg COD]	82,9*	%
Sludge production in digestion: <7%	<2	%
CH_4 content in biogas: >60%	57.4	%
H_2S content in biogas: <250ppm	<250	ppm
OLR COD: > 7 kg /(m3*d)	2,5	kg/(m3*day)
Water quality ex Effluent Treatment plant: COD < 100 mg /l	<100	mg/l
Boiler thermal efficiency: >92%	>95**	%
Gas engine overall efficiency >86%	>90%***	%
Electricity consumption ETP: <2,2 kWh/kg COD converted	2.23	kWh/kg COD

Glycerine digestion results [1 June 2016 – 1 July 2017]

Boiler efficiency data

The data file mentioned above does not contain information on the performance of the boiler after the modifications that took place in 2013-2014 and are part of the Quarterback project. To validate and monitor boiler performance improvements, both for technical and economical purposes, the Croda Gouda financial team compiles a monthly report containing all necessary data. Addendum C shows the relevant data used for boiler efficiency validation here, containing monthly data from the financial reports from June 2103 to July 2017.

Boiler efficiency was calculated on a monthly basis as is also done for regular monitoring. The efficiency is expressed here in its simplest form:

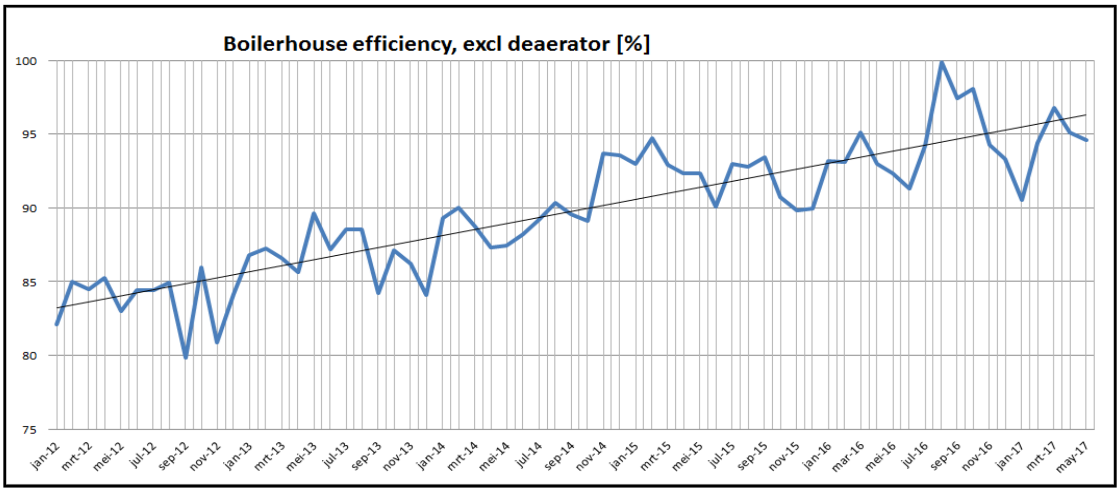
$$\text{Thermal efficiency } \eta = \text{Steam output [MJ] / (Water + Fuel input) [MJ]}$$

The output is defined by the mass of steam produced at a specific enthalpy of 2782,5 MJ/ton.

The net steam mass produced is calculated by reducing the gross boiler output with the steam taken of this flow and sent to the deaerator where the boiler feed water is stripped from oxygen prior to pumping into the boiler. Thus, the deaerator steam consumption is considered as a loss.

The input is the sum of the natural gas and biogas flows to the boiler, with natural gas expressed as standard Dutch gas, having a calorific value 31,65 MJ/Nm3 and biogas valued at average 21,0 MJ/Mn3 as measured by the on-line analyser installed in the biogas treatment system. The enthalpy of the feed water sent to the boiler is also added to the input.

Based on these calculations, the progress with improving the boiler conversion efficiency is shown in the graph below. Besides sometimes significant variations in efficiency, caused by operational factors like the average boiler steam load, the trend line shows an increase of efficiency from 83,5% to 96,0%. The project objective was to increase efficiency with 10%, so this objective was achieved.



Boiler efficiency improvements 2012 – 2017

Action C2. Validation of socio economic impact on the local economy and population

Socio-economic indicator	When?	Where?	Who?	What?	How?
SHE incidents	Continuous	Croda Incident Reporting	SHE Manager	All safety and environmental incidents	In CIR system via Intelex
Odour and noise complaints	Continuous	QA/Complaints reporting	Shift Manager	Complaints received from neighbourhood	Sustainability review and reporting
Safe working hours ratio	Quarterly	Croda Group central reporting	Group SHE Manager	Quarterly registration of hours worked by own Croda staff and contractors	On-site presence recorded via security desk
Quarterback dissemination	Continuous	Project database	Project Co-ordinator	Powerpoint presentations or articles	Copies of all documents
Quarterback website	Regular updates	Project website	Project Co-ordinator	Website visits	Website statisctics
Education	Regular updates	HR department	Training co-ordinator	Record of what school visited, when and how many attended	Departmental records
Open Day	2018	Croda Gouda site	Open Day team	Number of visitors	Sustainability records

Croda in Gouda is formally certified as per the ISO9001, ISO14001 and OHSAS18001 quality systems. The latter two qualifications are specifically targeted on HSE aspects and validation of the above C2 indicators (except for Open Day visitors) is covered by the audits done prior to (re)certification. Addendum B shows copies of the Croda Gouda certificates for ISO 14000 and OHSAS18001. Hence, in this report no further validation on the C2 indicators is described.

Longer term view.

Croda embraces the concept of sustainability, not only for their products based on natural raw materials but also for their production facilities. The Gouda manufacturing site started in 1858 at the outskirts of the town of Gouda but has long since been enclosed by housing, public buildings and other industry. The relation with the local population such as the direct neighbours, but also with the City Council has always been and will always be of crucial importance for the longer term future of the site.

Thus, active socio-economic relations when it concerns potential safety and environmental incidents, actual emissions and receiving local visitors remain crucial to that future. All complaints are formally registered and handled upon instantaneously by the shift teams. All incidents are recorded, investigated and action is undertaken where applicable to prevent re-occurrence. The local community will receive feedback when necessary.

To ensure the people working for or at Croda will go home safely after each work day, safety performance is closely monitored and continuously improved by Management. Part of the safety improvement program is to measure key parameters that indicate performance in that area.

All monitoring actions described above in both C1 and C2 will remain in place for the future. Based on this monitoring and on the present validation and evaluation results, further research will be done in identifying the digestion stability at higher temperatures, additional cooling facilities will be installed, odour emissions will be further reduced by installing scrubber facilities and biogas system reliability will be improved to increase effective bioga usage.

The production facility that was installed will have a technical lifetime of at least 15 years and more likely 25 years or higher. Collecting performance data will continue to ensure proper technical and economic performance.

For certain the EU and the NL Government will continue to enforce monitoring of energy consumption and related emissions in the foreseeable feature. Croda in the Netherland will formally accept further reductions of energy consumption and GHG emissions, not only because of legislation but also as part of the Croda world-wide sustainability program. It is possible that further energy reductions will make use of the experience and know-how gained by project “Quarterback”. There may be other processing side-streams that at present are treated as waste but that can be used as an energy source by converting organic material into methane for fuel. A review of potentially suitable side-streams would have to be done to identify such materials. If such materials are found further laboratory tests will have to be done to suitability for anaerobic digestion.

Performance against the objectives mentioned in the introduction will be evaluated on a monthly basis via the monthly site financial reporting system. That report summarises primary energy consumption, conversion efficiency and performance against the standards and the monthly budget. Consequently, energy and environmental performance is reported to Croda International of a quarterly and yearly basis. This system allows monitoring and evaluation of progress in reducing the environmental impact of the production site. Examples of longer term progress measurement, in this case of site CO2 emission and boiler efficiency performance, are shown below. This type of reporting will continue to be prepared in the future

ADDENDUM A LeAF Validation report

Performance validation of glycerine digesters

Commissioned by Croda

LIFE13/ENV/UK/000401 Quarterback Validation report

Ref: LeAF16070
Wageningen
21-8-2017

Title:	Performance validation of glycerine digesters
Status:	Final
Date:	21-8-2017
Client:	Croda Nederland b.v. Danny Zwakhals (Danny.Zwakhals@croda.com)
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LeAF project number:	16070

Table of Contents

1. Introduction 1
2. Validation approach 2
2.1 Evaluation period and performance goals 2
2.2 Available data 2
2.3 Background on anaerobic digestion 3
2.4 Determining the COD conversion efficiency 3
2.5 Sludge production 4
3. Performance evaluation 6
3.1 Glycerine conversion efficiency 6
3.2 Mass balance 7
3.3 Differences between digesters 8
3.4 Effect of operational problems 8
4. Conclusions 9
5. Recommendations 10
5.1 Operational stability 10
5.2 Measurements: parameters and frequency 10
5.3 Data collection files 11
Annex 1 – Background information on anaerobic digestion 12

Introduction

In 2016 Croda built an installation for anaerobic digestion of glycerine from splitters at its Gouda site. Digestion takes place in two stirred tanks, which have been started up in May/June 2016.

According to the digester design documents, laboratory tests indicated a 92-94% conversion efficiency of COD into methane. A validation programme is needed to assess full-scale conversion efficiency under actual conditions. The business case for the project was calculated based on an assumed glycerine to methane conversion efficiency of 90%, this is to be verified during the validation period.

Especially the solid organic matter in the effluent leads to higher processing costs. For this reason also the sludge production is part of the validation programme. The design assumption is that 5% of the COD is converted into sludge. This is to be verified during the validation period.

The total validation period was originally planned to cover one year. However, because of operational setbacks it took longer than expected to obtain representative data, resulting in a limited period of usable data.

Validation approach

Evaluation period and performance goals

The validation programme has the objective to verify whether the digester performance is in accordance with the design expectations. The performance is expressed as the percentage of sweetwater COD that is effectively converted into methane.

During the design phase the expected performance was indicated as 90% conversion of influent COD into methane and operation at 7.5 kg COD/m^3.d. The observed performance will be compared to these values.

The period of observation was June 1st 2017 until July 16th 2017. The digesters have been evaluated as if they were one large digester, as the received data file was organised in that way with respect to the digester feed data, the methane % in the biogas and the biogas production evaluation.

Available data

The operators regularly take samples for laboratory analyses of the digester content. In addition there are flow meters for influent and biogas and for some parameters the digesters are equipped with online monitoring. Table **Error! No text of specified style in document.**-2, Table **Error! No text of specified style in document.**-2 and Table **Error! No text of specified style in document.**-3 below show the parameters that are present in the data files received for the validation purpose.

Table **Error! No text of specified style in document.**-1 Influent (sweetwater) parameters registered in the received data file.

Parameter	Unit	Type of measurement	Remarks/questions
Flow to digesters	ton/h	Flow meter	Measured inline, registered daily
Flow to Voltz	ton/h	Flow meter	Measured inline, registered daily
Glycerine content	%	Laboratory analysis	Once a week, sometimes more
COD	mg/l	Laboratory analysis	Less than once a week

Table **Error! No text of specified style in document.**-2 Digester parameters (= effluent) registered in the received data file.

Parameter	Unit	Type of measurement	Remarks/questions
Temperature	°C	Sensor in digester	Measured inline, registered almost daily
pH	-	Laboratory analysis	Irregularly measured, some weeks every day
FOS	mg/l	Laboratory analysis	Daily
TAC	mg/l	Laboratory analysis	Daily
Dissolved COD	mg/l	Laboratory analysis	Less than once a week
Organic acids	mg/l	Laboratory analysis	Irregularly measured, some weeks every day

NH_4-N	mg/l	Laboratory analysis	Irregularly measured, some weeks every day
Dry matter	g/l	Laboratory analysis	Not measured

Table **Error! No text of specified style in document.**-3 Biogas parameters registered in the received data file.

Parameter	Unit	Type of measurement	Remarks/questions
Flow VS2000	m^3/h	Flow meter	Measured inline, registered daily
Flow VS3000	m^3/h	Flow meter	Measured inline, registered daily
Flow VS4000	m^3/h	Flow meter	Measured inline, registered daily
Flow to boiler	m^3/h	Flow meter	Measured inline, registered daily
Flow to gas engine	m^3/h	Flow meter	Measured inline, registered daily
CH_4	%	Sensor in biogas line	Measured inline, registered daily
H_2S	ppm	Sensor in biogas flow	Registered irregularly

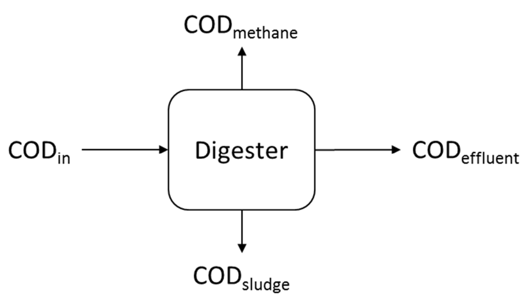
Sweetwater COD values were not measured daily, and proved to be difficult to measure. Based on the available data on COD concentration and on the glycerine content it was decided by Croda to assume for all days an average value of 200 g COD/l.

Background on anaerobic digestion

The anaerobically biodegradable COD fed to the digesters is converted by the biomass into different intermediate products and ultimately methane. Different processes take place, each performed by different groups of micro-organisms. For this performance evaluation it is assumed that the reader has knowledge on anaerobic digestion. See Annex 1 for complementary background information.

Determining the COD conversion efficiency

To be able to determine the conversion efficiency, a COD mass balance is made. This is done by calculating the total ingoing and outgoing COD amounts (mass/day). The influent COD is leaving the reactor in three flows: effluent COD, biogas COD and sludge COD.



Ideally the balance is a perfect COD_{in}=COD_{out}. However, in practice a 100% fitting balance is never possible. Reasons for this are:

- The relevant parameters are not continuously measured and/or registered, and therefore variations are not detected,
- Biological processes always present additional variations,
- Every measurement has its accuracy,
- It is very difficult to measure the sludge COD (see also the next section).

In anaerobic digestion often performance variations of up to 10% are observed, simply because it concerns biological processes. The expectations with respect to accuracy of the COD balance should take this into account.

The demonstration period officially started in June 2016. For validation purposes it was decided to include the measurements taken in the month of June 2017, plus the first two weeks of July 2017. This is a representative period in which the digesters were running in stable operation. In the months before there were large performance fluctuations because of start-up issues of the digesters and unstable sweetwater production.

Sludge production

The sludge contains active biomass (microorganisms), dead biomass, and degradable and inert solids originating from the feed. As mentioned previously, it is a challenge to accurately monitor the sludge production. In theory a CSTR-type digester is ideally mixed, which means that the effluent is representative for the entire reactor contents. However, in practice the lower part of the digester always contains denser sludge than the top part and if heavy inert solids enter the reactor these accumulate on the bottom. Accumulated heavy sludge should be extracted before it occupies a too large part of the digester volume.

Sludge is thus exiting the digester in two ways and for a fitting COD balance both flows should be included in the calculation of the sludge production: sludge contained in the effluent and periodically removed accumulated solids. The accuracy of the calculation heavily depends on how representative the analysed samples are for respectively the mixed reactor contents and the accumulated solids.

Both values are needed to determine the complete sludge production. The obtained value is then compared to the influent COD load to calculate the % of input COD that can be attributed to sludge production (either through conversion into biomass or accumulation on the bottom).

When no reliable sludge production data are available, usually it is assumed that the difference between COD_{in} and COD_{out} is equal to the sludge production, as long as that approach results in an acceptable value.

For the Croda digesters, as of yet no usable sludge measurements are available. The dry matter content is analysed infrequently, and the variations in the available measured concentrations are illustrative for the difficulty in measuring this parameter: e.g. 0.5% in both digesters on 15-6, compared to 0.9% in VS2000 and 1.2% in VS3000 one day later on 16-6. Seeing that the other parameters do not present large differences, this is a too large difference to occur naturally with only one day apart. Aspects affecting the measured concentration could be e.g. the sampling moment (effect of differences in mixing speed or mixing intervals), sample handling (mixing of digester sample before taking the subsample for analysis) or analysis errors.

Performance evaluation

Glycerine conversion efficiency

The Croda digesters receive sweetwater, containing 14-16% glycerine and small amounts of other residues from splitting fats and oils. On average the feed has a COD concentration of 200 g/l. Based on laboratory tests it was expected that over 90% of the glycerine COD would be converted into methane, at an organic loading rate of 7.5 kg COD/m^3.d.

Over the validation period of 1-6-2017 until 16-7-2017 for each day the produced amount of methane was compared to the COD load fed to the digesters. There were large fluctuations in conversion efficiency. This can be clearly seen in Figure 1 and Figure 2, comparing the input COD load to the total methane production.

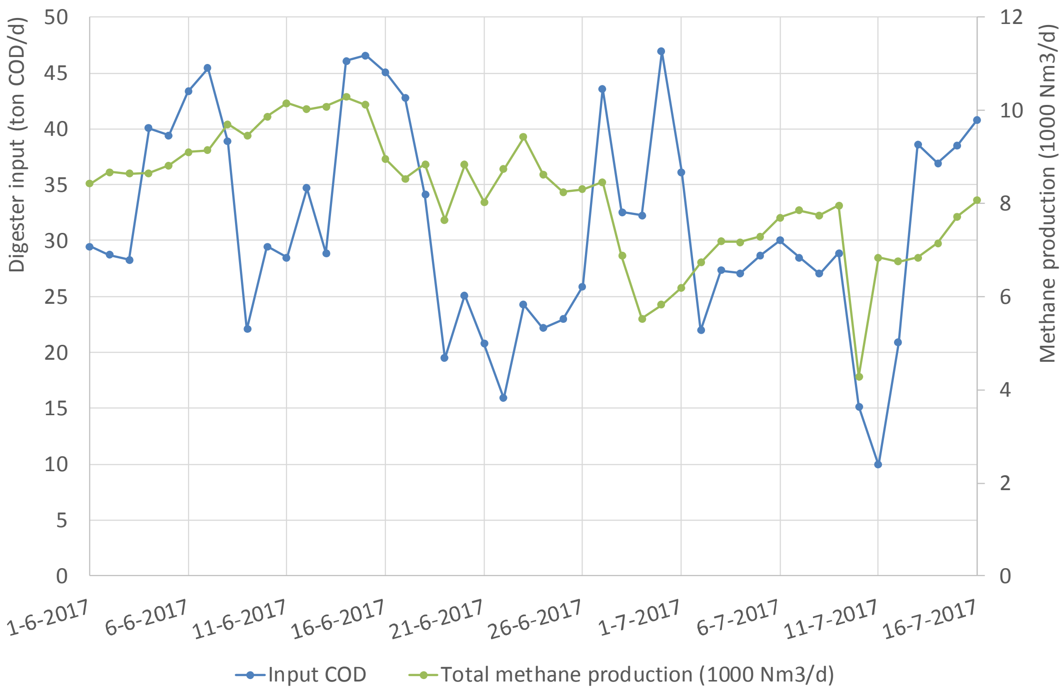


Figure 1. Digester input (COD load) compared to the total methane production.

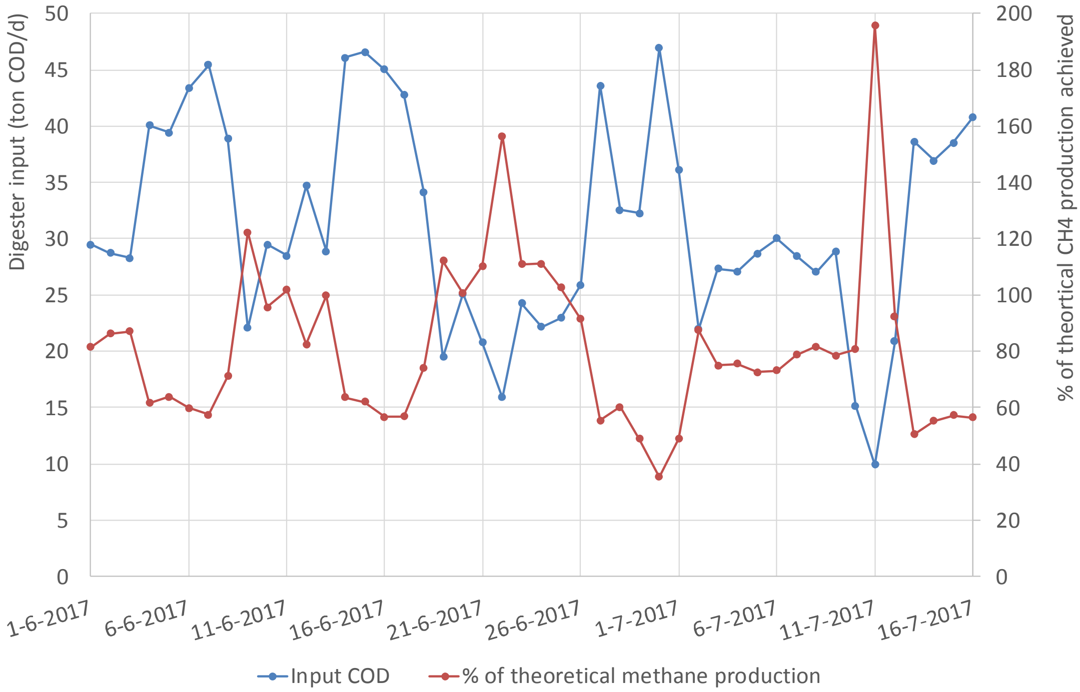


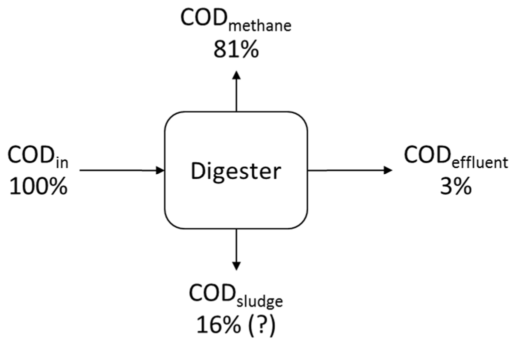
Figure 2. Digester COD load compared to the achieved % of theoretical methane production from input COD.

It can be seen that the methane production does not really follow the COD feed, and that the produced methane as percentage of the theoretical production shows a pattern that is the opposite of the fed COD load. At higher loads the production drops, whereas the observed amount of gas is sometimes more than 100% during periods of lower loading.

For high COD loads, the theoretically possible methane production is also high. However, these high expectations are not met. Apparently during large feeds the capacity of the microorganisms is exceeded, which means that not the whole feed could be degraded. This results in efficiencies of even below 50%. During low COD loads the expected methane production is lower. However, the non-consumed residues of the higher load are also consumed, giving impossible efficiencies of up to 200%.

Mass balance

When averaging the daily results, the methane production corresponds to 81.3% of the input COD. The digester effluent or digestate is taken to be representative to the digester contents (as they are CSTRs). Apart from sludge biomass it contains residues of the feed (either as glycerine or as intermediates). Assuming there are no solid input residues, the dissolved COD in the effluent should be representative for the non-converted input COD. On average, the amount of dissolved COD in the effluent is 3% of the influent COD. No information is available on the sludge production. Assuming this corresponds to the missing fraction, the following overall mass balance is obtained:



The apparent sludge production of 16% is relatively high but falls within the range for overall anaerobic digestion processes including acidification and methane production. Biomass yields in anaerobic digestion vary between 0.05-0.15 g VSS/g COD, or 7-21% of input COD taking the conversion factor of 1.4 g COD/g VSS for sludge biomass.

Looking at the organic loading rate to the digesters over the validation period of 1-6-2017 until 16-7-2017, this was on average 4.5 kg COD/m^3.d with minimum and maximum values of respectively 1.4 and 6.7 (assuming 7000 m^3 digester volume.). The fluctuations in organic loading resulted in large methane production fluctuations as previously shown in Figure 1 and Figure 2. The effluent dissolved COD value remained more constant, between 1,5% and 8% of influent COD.

Differences between digesters

Although they are fed at the same OLR, the two digesters show a large difference in performance. VS2000 performs significantly better than VS3000. A first analysis of only VS2000 showed that the conversion efficiencies in that digester did reach on average 90% of the theoretical production from the feed. This is assuming it received 50% of the sweetwater flow, and assuming the methane % of the biogas was the same as in the overall biogas. In the mass balance, sludge production would account for only 7%.

Effect of operational problems

During the observed period, there were two main operational problems causing unstable operation and therefore suboptimal performance. One is the already mentioned fluctuations in organic loading rate, between 1.4 and 6.7 kg COD/m^3.d. this resulted from variations in upstream splitter operation, and lack of experience in optimising the use of the influent buffer. Being used to chemical processes, it takes time for the operators to learn and experience how to optimise the combination of the splitter operations, sweetwater buffer and digesters. In addition, the digesters experience a problem of heat production from glycerine conversion. During the design phase it was noted that glycerine is highly degradable and has a high energy content. However, it was not foreseen that the heat produced from the conversion would be sufficient to significantly increase digester temperature. This effect is seldom reported. Anaerobic digestion takes place within either a mesophilic or thermophilic temperature range. The microorganisms operating within these ranges are different groups. At temperatures increasing above the mesophilic range, as happened at Croda, the sludge biomass cannot function optimally.

Conclusions

During the observed period, the digester performance did not meet the design goals of 90% COD conversion into methane and operation at an OLR of 7.5 kg COD/m^3.d. However, those design goals supposed stable operation.

As shown in chapter 0, the digester COD loading greatly fluctuated, resulting in large variations in methane production. Also, there was the added complication of rising temperatures. Temperatures increased from 40.4°C on June 1st to 46.6 on July 16th, above the mesophilic optimum and below the thermophilic optimum.

At unstable operation an average conversion efficiency of 81% of input COD into methane was achieved. OLR fluctuated between 1.4 and 6.7.

It is expected that performance will increase once the digesters are being operated at a stable OLR and stable temperature, either within mesophilic or within thermophilic range. Whether the digesters will be able to run at 7.5 kg COD/m^3.d and 90% conversion efficiency is impossible to predict.

Recommendations

Operational stability

The digesters will need to be operated at a much more stable OLR than presently is the case. For this, different people/departments at Croda will need to work together to balance their activities, including at least the splitter operations, sweetwater buffering and digester feeding. At stable feeding, the different groups of organisms in the sludge biomass will be better able to establish a stable community.

At present a transition is taking place towards full thermophilic operation. A stable temperature regime will add to process stability, but thermophilic digesters are known to be more sensitive to process disturbances – an extra reason to optimise and stabilise the digester input.

Measurements: parameters and frequency

Measurements should be done in such a way that the monitoring results can be used for directing the daily digester operation, and for performance evaluation. For this a certain level of detail is needed (number and types of parameters, measurement frequency), measurements should be as accurate as possible (good sampling and analysis practices), while staying within the practical limits present at the site (availability and motivation of operators, laboratory equipment).

Currently, the monitoring data file presents irregular data registry and large gaps for some of the parameters. It is recommended to evaluate the sampling and analysis procedures to find out which parameters and frequency are optimal to comply with the monitoring objective while being manageable for the operators[1].

An example: for the FOS/TAC ratio determination organic acids are measured (FOS). In addition, organic acids are measured using cuvette tests. One would expect the results to be similar, or at least to follow the same tendencies. However, the resulting values are very different and follow different patterns. This can be due the differences between the two analysis methods, or due to analysis errors. Whatever the reason, if these measurements are to be used for digester operation control it is necessary to:

- Understand the purpose of measuring the parameter (or both),
- Make sure the sampling, sample preparation and analyses are done correctly,
- Understand the differences between the methods if both are used,
- Define how the results should be interpreted for digester operation control.

[1] It is important that the operators understand the purpose of sampling and analysis, for example through a workshop on the basics of anaerobic digestion or a background document.

Data collection files

The data collection files should contain the measured parameters and make interpretation easy. They should be designed for easy registering of data, either manually or taken from online monitoring equipment. For interpretation it is good to directly calculate the important control parameters, such as FOS, FOS/TAC and OLR and also plot those in a graph to make is easier to see tendencies.

The volumetric organic loading rate (OLR, kgCOD/m^3.d) is one of the most important parameters in wastewater treatment. Variations in OLR can almost always be directly linked to process performance. It is recommended to use the data collection files to automatically calculate the OLR:

$$OLR = \frac{Q \cdot C}{V}$$

- OLR = volumetric organic loading rate (kgCOD/m^3.d)
- Q = flow rate (m^3/d)
- C = concentration (kgCOD/m^3)
- V = reactor volume (m^3)

In agricultural CSTR-type digesters in the Netherlands OLR is not used that much for process control, in comparison to FOS/TAC. However, at Croda the CSTR is a wastewater treatment plant and not a slurry digester. Glycerine is a fast degrading substrate, and the sweetwater is highly concentrated. The risk of organic overloading is high, and FOS/TAC can show a normal value while the process in fact is already becoming unstable. Keeping an eye on OLR can be of help.

Annex 1 – Background information on anaerobic digestion

The anaerobically biodegradable COD fed to the digesters is converted by the biomass into different intermediate products and ultimately methane. Different processes take place, each performed by different groups of micro-organisms. The figure below shows an overview of the different anaerobic conversion processes and the order in which they take place to ultimately be converted in methane.

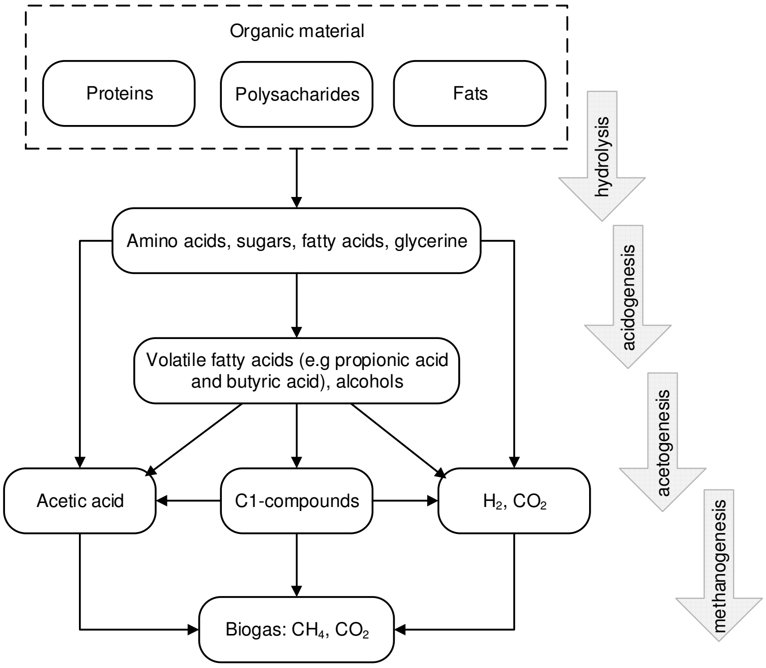


Figure: Anaerobic conversion of substrates

The different steps shown in the figure are:

1. Hydrolysis: transformation of complex molecules (solid organic matter) in soluble organic matter,
2. Acidogenesis (1st part of the acidification): formation of different shorter fatty acids and alcohols,
3. Acetogenesis (2nd part of the acidification): formation of mainly acetic acid,
4. Methanogenesis (methane formation)
    a. from acetic acid,
    b. from hydrogen and carbon dioxide,
    c. from C1-compounds, such as methanol and formate.

Of course in the digesters these processes take place at the same time, with intermediates and new glycerine continuously becoming available for conversion. To obtain a properly functioning anaerobic digestion it is important that the basic processes are well-balanced. The different processes are in fact dependent on each other: they produce each other's substrates and consume each other's products. Anaerobic digestion proceeds well when the products of each step are transformed immediately in the next step. Furthermore, the combination of processes cannot proceed faster than the slowest process involved, and when one of the processes is disturbed the overall digestion is negatively impacted. Generally, the hydrolysis is the slowest process, that is: the rate-limiting step.

With fast degrading substrates like glycerine, it is easy to overload the system. When more organic acids are produced than can be consumed, the pH drops and the methane producing organisms are inhibited. This results in less acids being consumed, the digester contents becoming more acidic, more inhibition, etc.: a vicious circle ultimately leading to complete acidification of the digester and standstill of biogas production. In the worst case the toxic effect is so strong that reinoculation is required.

Different groups of microorganisms have adapted to different temperature ranges to grow in, and each group has its own optimum temperature. Within the range of a group each reaction has its optimum temperature with maximum activity. Above or below the optimum temperature the reaction rate decreases. At temperatures just a few degrees above the optimum decay starts for most bacteria, although some are relatively tolerant. At lower temperatures normally the activity goes down but the organisms do not die. For anaerobic digestion bacteria are divided in three groups, each with their own temperature optimum:

- 0-20°C: psychrophilic micro organisms
- 20-40°C: mesophilic micro-organisms
- above 40°C: thermophilic micro-organisms. Thermophilic digestion takes place at a maximum of 55-60°C. However, bacteria exist that can grow at temperatures of 120°C.

The graph below is meant to give a general idea of the differences between the three main groups, without going into detail. For each micro-organism the rates are different, which makes it impossible to include numbers on the y-axis.

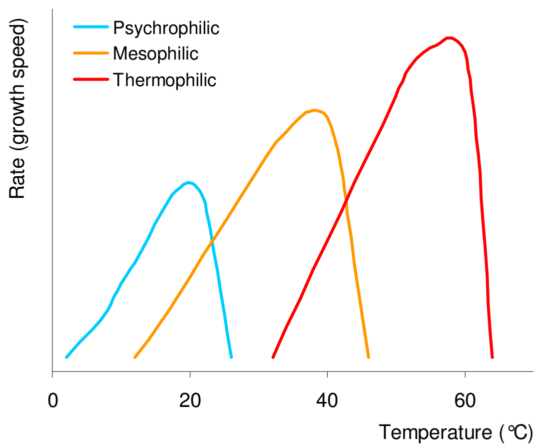


Figure: General indication of temperature ranges for bacterial growth

Within each temperature group we can see that the rate increases with increasing temperature, and when passing the maximum there is a rapid decline. As stated before, at lower temperatures micro-organisms are merely less active, but at temperatures above their optimum they will die quite rapidly. In general, the maximum rates of psychrophilic organisms are lower than the maximum rates of mesophilic organisms, which are generally lower than for the thermophilic organisms. It cannot be generalised for example how much higher the thermophilic rate is when compared to mesophilic conditions, the figure should not be taken too literally.

The mentioned groups of micro-organisms are very different. Therefore a digester cannot be switched from one operating temperature range to the other without loss of activity. When a lasting temperature change is applied, other microorganisms will start growing to take over the process.

ADDENDUM B ISO14001 and OHSAS18001 Certificates by BSI

bsi.

By Royal Charter

Certificate of Registration

ENVIRONMENTAL MANAGEMENT SYSTEM - ISO 14001:2015

This is to certify that: Croda Nederland B.V.
Buurtje 1
2802 BE Gouda
The Netherlands

Holds Certificate No: **EMS 565278**

and operates an Environmental Management System which complies with the requirements of ISO 14001:2015 for the following scope:

The manufacture and supply of oleo-chemicals and speciality chemicals derived from natural oils and fats to company and agreed specifications.

For and on behalf of BSI:

Andrew Launn - EMEA Systems Certification Operations and Compliance Director

Original Registration Date: 2010-12-23
Latest Revision Date: 2017-05-31

Effective Date: 2017-07-23
Expiry Date: 2020-07-22

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By Royal Charter

Certificate of Registration

OCCUPATIONAL HEALTH & SAFETY MANAGEMENT SYSTEM

This is to certify that: Croda Nederland B.V.
Buurtje 1
2802 BE Gouda
The Netherlands

Holds Certificate No: **OHS 565277**

and operates an Occupational Health and Safety Management System which complies with the requirements of BS OHSAS 18001:2007 for the following scope:

The manufacture and supply of oleo-chemicals and speciality chemicals derived from natural oils and fats to company and agreed specifications.

For and on behalf of BSI: Andrew Launn - EMEA Systems Certification Operations and Compliance Director

Original Registration Date: 2010-12-23
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Page: 1 of 1

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ADDENDUM C. Boiler performance data 2013-2017 (note: NG = Natural Gas, K10 = boiler)

Month	E power purchased [kWh]	E power purchased [GJ]	NG purchased for utilities [mn3]	NG purchased for utilities [GJ]	NG consumption gasengine [mn3]	NG consumption gasengine [GJ]	Biogas consumption [mn3]	Biogas consumptio n [GJ]	Of which biogas to boiler[mn3]	Of which biogas to boiler[GJ]	NG purchased for K10 [mn3]	NG purchased for K10 [GJ]	HP steam [ton]	HP steam [tonx100]	Gas/steam ratio K10 [mn3/ton]
jun-13	2850000	10260	1378124	43618							1378124	43618	15181	1518100	90.78
jul-13	3263000	11747	1705340	53974							1705340	53974	19292	1929200	88.40
aug-13	3383000	12179	1641919	51967							1641919	51967	18477	1847700	88.86
sep-13	3139087	11301	1740460	55086							1740460	55086	18602	1860200	93.56
okt-13	3346000	12046	1799234	56946							1799234	56946	19873	1987300	90.54
nov-13	2876000	10354	1525746	48290							1525746	48290	16359	1635900	93.27
dec-13	3065000	11034	1961430	62079							1961430	62079	20653	2065300	94.97
jan-14	3470000	12492	2024990	64091							2024990	64091	22906	2290600	88.40
feb-14	3190000	11484	1836513	58126							1836513	58126	20508	2050800	89.55
mar-14	3292366	11853	1829184	57894							1829184	57894	20502	2050200	89.22
apr-14	2955293	10639	1503074	47572							1503074	47572	16706	1670600	89.97
mei-14	3336119	12010	1762515	55784							1762515	55784	19523	1952300	90.28
jun-14	2797342	10070	1544420	48881							1544420	48881	17036	1703600	90.66
jul-14	3316475	11939	1707912	54055							1707912	54055	19235	1923500	88.79
aug-14	3233194	11639	1710452	54136							1710452	54136	19323	1932300	88.52
sep-14	2931601	10554	1512052	47856							1512052	47856	16715	1671500	90.46
okt-14	2663793	9590	1490966	47189							1490966	47189	16614	1661400	89.74
nov-14	3208049	11549	1800295	56979							1800295	56979	21067	2106700	85.46
dec-14	3219743	11591	1975246	62517							1975246	62517	23170	2317000	85.25
jan-15	3365879	12117	2024169	64065							2024169	64065	23098	2309800	87.63
feb-15	3092885	11134	1808422	57237							1808422	57237	21240	2124000	85.14
mar-15	3167160	11402	1754654	55535							1754654	55535	20878	2087800	84.04
apr-15	3007375	10827	1546493	48947							1546493	48947	18453	1845300	83.81
mei-15	3099306	11158	1686243	53370							1686243	53370	19917	1991700	84.66
jun-15	2331538	8394	1362931	43137							1362931	43137	15126	1512600	90.11
jul-15	2714309	9772	1550807	49083							1550807	49083	18198	1819800	85.22
aug-15	3010315	10837	1792896	56745							1792896	56745	20927	2092700	85.67
sep-15	3065564	11036	1739350	55050							1739350	55050	20512	2051200	84.80
okt-15	2849896	10260	1387125	43903							1387125	43903	15901	1590100	87.24
nov-15	3054082	10995	1635263	51756							1635263	51756	18966	1896600	86.22
dec-15	3214580	11572	1846716	58449							1846716	58449	21390	2139000	86.34
jan-16	2988629	10759	1798083	56909							1798083	56909	20951	2095100	85.82
feb-16	3212933	11567	1775428	56192							1775428	56192	21146	2114600	83.96
mar-16	2612721	9406	1422992	45038							1422992	45038	16798	1679800	84.71
apr-16	3078036	11081	1565602	49551							1565602	49551	18798	1879800	83.29
mei-16	3033186	10919	1530711	48447							1530711	48447	18338	1833800	83.47
jun-16	2436684	8772	1312864	41552							1312864	41552	15289	1528900	85.87
jul-16	2412935	8687	1814659	57434	78808	2494	27330	865			1735851	54940	19942	1994200	87.04
aug-16	2202055	7927	1575645	49869	107430	3400	112164	3550			1468215	46469	17866	1786600	82.18
sep-16	2018010	7265	1249365	39542	86184	2728	47393	1500			1163181	36815	13872	1387200	83.85
okt-16	1873938	6746	1615131	51119	139796	4425	106445	3369			1475335	46694	17534	1753400	84.14
nov-16	2161044	7780	1798592	56925	109685	3472	124961	3955			1688907	53454	20251	2025100	83.40
dec-16	1711710	6162	1795924	56841	194954	6170	123633	3913			1600970	50671	19372	1937200	82.64
jan-17	2407562	8667	1913910	60575	106702	3377	251125	5390	62329	1348	1807208	57198	23257	2325700	79.54
feb-17	2459004	8852	1584561	50151	53471	1692	230117	4867	119268	2534	1531090	48459	19933	1993300	80.83
mrt-17	2462022	8863	1689682	53478	87814	2779	327932	6887	134755	2830	1601868	50699	21166	2116600	79.91
apr-17	2396618	8628	1639167	51880	118357	3746	146656	3080	26166	549	1520810	48134	18992	1899200	80.99
may-17	1649548	5938	1320035	41779	97342	3081	268612	5641	45735	960	1222693	38698	14756	1475600	84.92
jun-17	1538230	5538	1185442	37519	37127	1175	417620	8770	37250	782	1148315	36344	14237	1423700	82.39
jul-17	2153331	7752	1493125	47257	58487	1851	398,218	8363	27492	577	1434638	45406	17778	1777800	81.72