

## **Pyrolysis – a way of recovering energy from wastewater sludge from milk processing factories**

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### **Abstract**

In Ireland the majority of the sludge from the treatment of wastewater in milk processing plants is land spread. Some sludges are sterilised and stabilised by composting and then returned to the land. Drawbacks of land spreading include local oversupply due to high transport costs which results in sludge being spread on lands in the vicinity of the dairy factories. Local oversupply can lead to accumulation of certain substances in soil through annual application over many years. Therefore, in the long term, there is a need to find an alternative way to recover energy and nutrients from sludges generated from dairy processing. Pyrolysis can be an interesting option which allows energy recovery in the form of a high calorific value pyrolysis gas and a char may be used as soil amendment or an adsorbing media.

In this study pyrolysis of dried dairy sludge samples was carried out using TGA and a simple laboratory fixed bed reactor. Characterisation of the feedstock and pyrolysis chars was performed and the pyrolysis gases were analysed. The mass balance information obtained from the fixed bed tests was used for an indicative energy balance for the pyrolysis products. A preliminary attempt was made to look at seasonal variability in the properties of sludge from milk processing factories and its effect on the distribution of the pyrolysis products.

### **Keywords**

Dairy processing sludge, pyrolysis, pyrolysis gas, DAF sludge, energy

### **1. Introduction**

The dairy industry accounts for approximately 30% of Irish agri-food exports, with 80 % of milk products being exported. In order to promote growth within this sector, the Irish government has adopted strategies that offer scope for significant expansion with the aim to increase milk production by 50% overall by 2020 using the average of the outputs from 2007 to 2009 as a baseline. An increase in primary production will inevitably lead to an increase in the generation of processing waste such as sludge from the treatment of wastewater from milk processing plants. The composition of dairy sludge depends on the type of products being manufactured and cleaning process deployed in the plant. In general there are two main types of sludge: chemical sludge which is a mixture of fat, grease, oil and suspended solid particles removed from raw effluent in the waste water treatment plant together with some proteins and minerals by dissolved air flotation (DAF) and biological sludge which is an organic material, containing suspended solids and non-biodegradable pollutants such as heavy metals resulting from biological aerobic, anaerobic or anoxic waste water treatment processes [1,2]. In Ireland the majority of the sludge is land spread, e.g. in 2004 around 120,661 tonnes of dairy sludge was land spread [3]. Some sludges are sterilised and stabilised by composting and then returned to the land. DAF sludge is sometimes used as a feedstock for anaerobic digestion, however the milk fat is not easily bio-degraded and causes technological issues [4,5]. When dairy sludges are used as an organic, nutrient rich fertilizer [6] a strict code of practice must be complied with for the spreading of organic dairy sludge once a Nutrient Management Plan has been approved by the Environmental Protection Agency [7]. Drawbacks of land spreading also include local oversupply due to high transport costs which results in sludge being spread on lands in the vicinity of the dairy factories. Local oversupply can lead to accumulation of certain substances in soil through annual application over many years. Energy is not recovered from the land spread dairy solids and from an energetic point of view the net calorific value of some dry dairy sludges can be compared with wood.

Therefore, in the long term, there is a need to find an alternative way to recover energy and nutrients from sludges generated from milk processing plants. Pyrolysis can be an interesting option which allows energy recovery in the form of a high calorific value pyrolysis gas. According to a recent study by Samolada and Zabaniotou [8] pyrolysis seems to be an optimal thermochemical treatment option compared to gasification and incineration.

Pyrolysis is a thermal decomposition of carbonaceous material in an inert atmosphere into gaseous, liquid and solid product. Pyrolysis gas contains the un-condensable low molecular gases like H<sub>2</sub>, CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, CO<sub>2</sub>. Pyrolysis liquid contains the condensable volatile compounds, water and water-soluble organics[9]. The solid residue obtained, namely char is comprised mainly of carbon and ash. Pyrolysis product yields are affected by the process conditions including temperature, reactor residence time as well as original feedstock properties. Slow pyrolysis is generally characterized by relative mild temperatures (350-700°C) and heating rates[8]. The low pyrolysis temperature is responsible for the absence of heavy metals in the pyrolysis gas, which remain trapped in the resulting carbonaceous char [10]. Pyrolysis gas can be used as a fuel in a boiler or gas engine. The char can be used either as a solid fuel or as a soil amendment while the uses for the liquid fraction are highly dependent on its composition.

This study is part of a project which investigates the potential of pyrolysis as a conversion technology for sludge from milk processing factories in the frame of state founded Dairy Processing Technology Centre. In this study samples of dairy sludges were pyrolysed using TGA in order to examine differences in the chemical composition of the tested samples and in a laboratory fixed bed reactor in order to measure the amount of pyrolysis products and determine their properties. A preliminary attempt was made to determine the suitability of the sludges for pilot scale pyrolysis trials.

## 2. Materials and Methods

Dairy processing sludge samples from three milk processing plants in Ireland are the focus of this work. The range of milk products produced by the dairy companies at the time when sludge sample were collected is presented in Table 1.

Table 1. Milk products produced by dairy companies.

Milk processing companies	Products				
Company 1 (Sludge 1)	Butter	Skim milk powder			
Company 2 (DAF Sludge 2)	Butter	Skim milk powder	Whey powders (acid)	Casein (acid)	
Company 3 (DAF Sludge 3)	Butter	Skim milk powder	Whey powders (sweet)	Casein (Rennet)	Cheese

The sludge samples were of two types: sludge after biological treatment processes with cationic polyelectrolyte addition to aid coagulation - Sludge 1 and two samples of sludge from a dissolved air floatation process - DAF Sludge 2 and DAF Sludge 3.

All sludge samples were bench dried at ambient temperature and then pyrolysed in a laboratory scale fixed bed reactor. The pyrolysis set-up consisted of a quartz tube reactor (I.D./O.D. of 45/50 mm and a total length of 600 mm) coupled with a condenser cooler and a twin-neck round-bottom receiving flask where the pyrolysis liquid was collected. The condenser outer jacket was cooled through circulation of a refrigerated liquid at -5°C. The outlet of the receiving flask was connected to a rubber tube fitted with a connector which enabled gas sampling or connection to an extraction hood, where the permanent gases were discharged. The quartz reactor was wrapped with a heating tape (Omegalux, USA) and two layers of woven high-temperature insulation were wrapped around the outside of the heating tape. An electro-thermal power regulator (Cole-Parmer, UK) was used to supply the heating tape with electricity. The heating section of the tube reactor was approximately 300 mm long. A batch of dried sludge in a steel-mesh basket was placed in the reactor, heated to 700°C, and kept at this temperature for 10 minutes during which the feedstock was pyrolysed. The product gas generated was cooled to room temperature while passing through the cooler, and a sample of gas was collected in Tedlar bags each minute. Then the heating jacket was turned off and the char was cooled to room temperature while still in

the reactor. The char yield was obtained as the ratio between mass of the char after pyrolysis and the initial sample mass. The vast majority of pyrolysis liquid was collected in the receiving flask; however, some of the oil/tar condensed on the cool parts of the experimental set-up. Therefore, in order to account for this fraction before and after each series of pyrolysis runs, the reactor with the heating tape and insulation, the receiving flask, the dry condenser, the rubber stopper and all of the connected glass ware were weighed and the mass of liquid fraction was obtained. The gas yield was calculated by the difference between the initial sample mass and the char and the pyrolysis liquid mass.

Thermo-gravimetric analysis (TGA) was performed in a PerkinElmer Pyris instrument. Approximately 15 mg of dried, ground and sieved to particle size below 50  $\mu\text{m}$  sludge sample was placed into an alumina pan without a lid and heated from ambient temperature to 900°C with a constant heating rate of 20°C/min under a nitrogen purge flow of 20  $\text{cm}^3/\text{min}$ . Analysis of proximate and ultimate properties as well as the calorific value of the dried dairy processing sludge and the pyrolysis chars were carried out by Celignis Analytical, Ireland. The proximate properties of the sludge samples were analysed according to BS EN 14774-1: 2009 (moisture content), BS EN 15403: 2011 (ash content) and BS EN 15402: 2011 (volatile matter content). The elemental composition (C, H, N, S) was determined using a Vario EL cube elemental analyser. The higher heating value (HHV) was measured with a Parr 6300 isoperibolic calorimeter and the corresponding lower heating value (LHV) was calculated. The pyrolysis gas composition ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{N}_2$ ,  $\text{O}_2$ ) was determined by means of gas chromatography (micro-GC, Agilent 3000) and was used to calculate its heating value.

### 3. Results

#### 3.1 Properties of dairy sludge

In Table 2 the properties of the different type of dried sludge are presented. In all tested sludge samples high volatile matter content (from 62 -77 wt. %) and low fixed carbon (2 – 7 wt. %) was observed. This indicates that during high temperature decomposition most of the organic content of the dried sludge will turn into vapours (non-condensable permanent gases and condensable compounds). The dried sludge samples have a relatively high net calorific values in the range of around from 17 to 25 MJ/kg. The nitrogen content is high, above 1.5 wt. %, and it is the highest is in Sludge 1 at 7 wt. %. High nitrogen content is one of the typical characteristics of dairy sludge resulting from biological and chemical treatment of defatted effluent [2]. The sulphur content of all sludge sample is in the range suitable for thermal processing. The content of major and minor elements in the sludge dry matter is reported in Table 3 and 4. High phosphorus content can be observed in all of them.

Table 2 Properties of different types of dried dairy sludge.

Properties, wt. %	Sludge 1	DAF Sludge 2	DAF Sludge 3
Moisture, ar.	86.50	67.60	94.54
Moisture, after bench drying	14.81	6.24	8.93
Ash content, db.	24.47	36.41	19.00
Volatile matter, db.	68.14	61.89	77.46
Fixed carbon, db.	7.39	1.70	3.54
LHV, MJ/kg db.	17.246	18.966	25.487
C, db.	40.92	43.31	54.90
H, db.	6.15	6.94	8.71
N, db.	6.95	1.63	2.37
S, db.	0.67	0.11	0.40
O, db.	20.84	11.60	14.62

ar. - as received, db. – dry basis

Table 3 Content of major elements in the tested streams in mg/kg of dry matter.

	Sludge 1	DAF Sludge 2,	DAF Sludge 3,

	mg/kg	mg/kg	mg/kg
Al	33223.2	3520.3	5889.8
Ca	22958.6	114114.7	20036.8
Fe	888.2	1006.0	2009.5
K	6054.7	1731.3	6032.9
Mg	1584.5	5141.5	1945.9
Na	18282.6	1788.1	9526.8
P	29601.6	39331.1	20692.4
S	56.1	-	-
Si	2995.2	80404.3	7384.4

Table 4 Content of minor elements in the tested streams in mg/kg of dry matter.

	Sludge 1 mg/kg	DAF Sludge 2, mg/kg	DAF Sludge 3, mg/kg
As	0.00	-	3.84
Ba	20.31	-	49.41
Be	0.00	-	-
Cd	0.00	0.00	25.25
Cr	12.83	11.74	14.27
Cu	14.43	57.08	0.00
Hg	0.00	-	0.00
Mn	40.60	20.12	13.17
Mo	3.21	41.30	
Ni	4.27	11.17	0.55
Pb	0.00	82.85	1.09
Sb	56.11	1.67	2.74
Se	0.00	4.47	120.78
Ti	62.52	100.00	0.00
V	2.14	4.47	0.00
Zn	24.05	125.17	25.80

### 3.2 TG data

Thermogravimetric analysis (TG), while measuring mass loss as a function of temperature, provides a useful insight into the thermal decomposition characteristics of materials. The TG profiles obtained during the programmed heating experiment for the dried sludge samples in an inert atmosphere is shown in Fig. 1. It can be seen from the thermograms that the main devolatilisation (pyrolysis) process occurred at temperatures below 600°C with 60 -70 % of mass reduction observed for all samples followed by a further gradual decrease in sample mass up to the final temperature. However, for DAF Sludge 2 a significant mass reduction (about 15 %) was also observed at a temperature of around 750°C.

Differential thermogravimetric analysis (DTG), which represents the rate of sample mass loss, reveals differences in the chemical nature of the tested sludge samples. The peaks in Fig. 2 exemplify the decomposition of certain components occurring at different temperatures because of intrinsic differences in the structure of these constituents. It was observed by Sunooj et al. [11] that the peak maximum temperature for cow milk protein decomposition occurs at 327°C while that for milk fat is at 413°C. Whereas Mocanu et al.[12] reported that decomposition of casein, main protein in milk, starts at temperatures above 176°C and proceeds in three stages up to 610°C with the peak maximum degradation at 310°C. In Fig. 2 the first peak at about 105°C originates from evaporation of moisture and is common for all sludge samples. The second peak at 322°C

(Sludge 1), 336°C (DAF S-2) and 292°C (DAF S-3) probably correspond to the decomposition of protein. From the DTG curve it can be concluded that the lowest content of protein is in DAF S-1. The decomposition events within the temperature range from 400 to 500°C most likely relate to the decomposition of fat contained in all types of sludge samples.

The fat content is evidently high for the two DAF sludge samples, but is the highest in DAF-S1. The major component of fat contained in dairy factory waste waters is triglyceride (98 %) while other components include phospholipids and sterols [5].

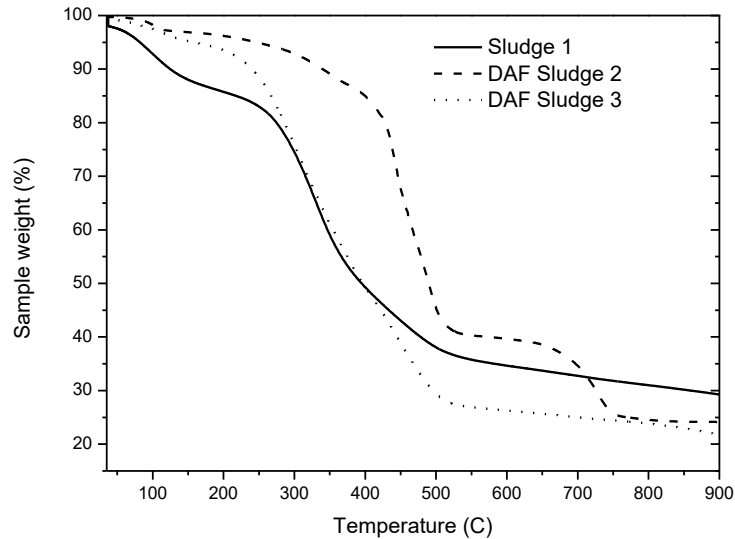


Fig 1. TG curves for dried dairy sludge.

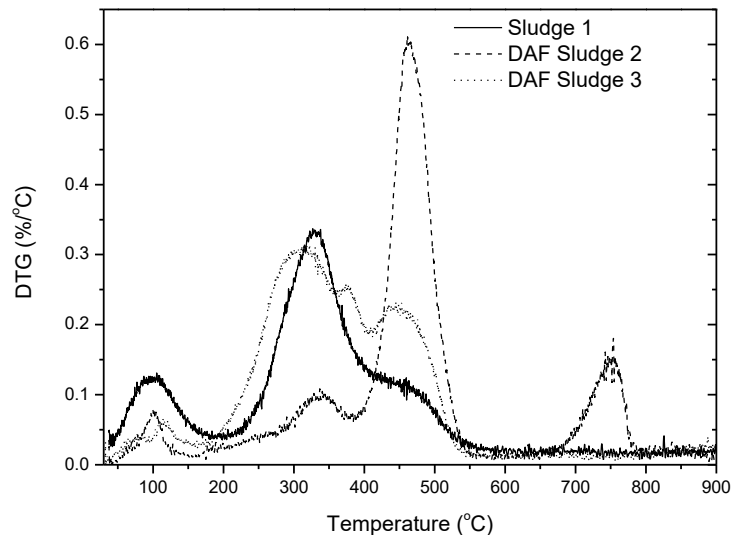


Fig 2. DTG curves for dried dairy sludge.

### 3.3 Fixed bed pyrolysis and its products

The average values and distribution of the pyrolysis products obtained in laboratory scale experiments are reported in Table 5 and in Fig. 4. Pyrolysis of dairy sludge produced a significant quantity of pyrolysis gas comprising of 59 % (DAF – S3) and about 50 % (Sludge 1 and DAF Sludge 2) of the initial residue mass. The remaining 50 % was more or less equally split between solid (19 and 27 %) and liquid (21 and 22 %) products

for DAF-S3 and Sludge 1, respectively. Whereas partitioning of solid and liquid pyrolysis products was slightly different for DAF-S2, with more solids (37 %) obtained due to a higher initial ash content (see Table 2) while the liquid fraction was lower (15 %).

The experimental uncertainty in the char yield was relatively low because the sludge sample and char were measured directly. In contrast the liquid yield had a greater uncertainty. Even though the whole experimental apparatus was weighed before and after pyrolysis in order to obtain the mass of the liquid fraction there was always some oil condensed in the gas sampling bags. This indicates that some pyrolysis products escaped the apparatus as vapours or aerosols. Thus, based on the conservation of mass, the measured liquid fraction should be considered the minimum. Consequently, as the gas yield is calculated by the difference between the solid and the liquid pyrolysis products and the initial sample mass, the gas yield should be considered the maximum value.

Table 5. Products distribution from pyrolysis of died dairy sludge samples. Mass balance.

Residue type, pyrolysis conditions 700°C, 10 min	Total mass of residue pyrolysed, g	Solid product (char + ash), wt. %	Liquid (oil+water) yield, wt. %	Gas yield, wt. %
Sludge 1	152	26.6 +/- 2.7	21.9	51.5
DAF-Sludge 2	1016	37.5 +/- 2.6	14.7	47.8
DAF-Sludge 3	137	19.4 +/- 2.8	21.5	59.1

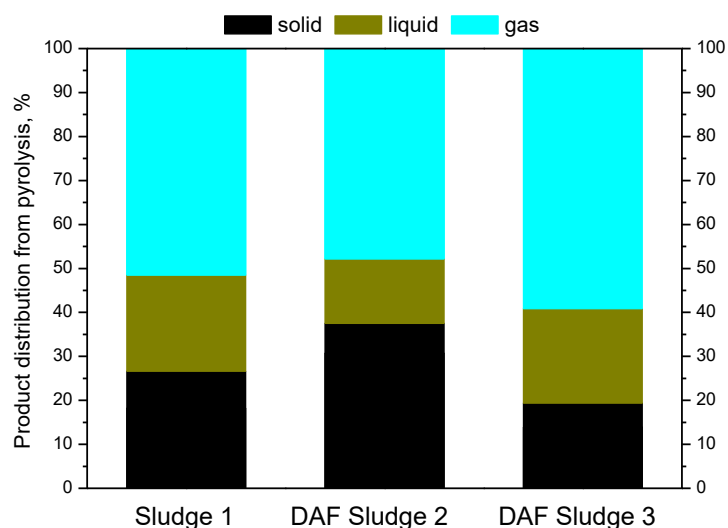


Fig. 4 Mass balance for pyrolysis products.

Table 6 Properties of solid residue from pyrolysis of dried dairy sludge samples.

Properties, wt. %	Sludge 1	DAF Sludge 2	DAF Sludge 3
Moisture, ar.	1.75	0.00	0.73

Ash content, db.	69.68	81.83	72.01
Volatile matter, db.	4.29	14.48	4.16
Fixed carbon, db.	26.03	3.69	23.84
LHV, MJ/kg db.	9.40	2.70	8.82
C, db.	26.26	10.11	24.51
H, db.	0.46	0.55	0.43
N, db.	2.85	0.39	1.51
S, db.	0.30	0.04	0.47
O, db.	0.45	7.07	1.07

ar. - as received, db. – dry basis

The proximate and ultimate properties of the solid pyrolysis products are presented in Table 6. The solid products, most often called pyrolysis chars, consisted mainly of ash at about 70 - 80 wt. %. For Sludge 1 and DAF-S3 a substantial amount of carbon was forming the carbonaceous structure of the char, with a fixed carbon content of 24 and 26 wt. %, respectively. Therefore, the net calorific value of these chars was relatively high at about 9 MJ/kg, whereas, the net calorific value of char from DAF-S2 was much lower at 2.7 MJ/kg with a corresponding fixed carbon content of 3.7 wt. %. The volatile matter content in chars from Sludge 1 and DAF-S3 was low at about 4 wt. % implying that almost complete decomposition of the organic matter occurred in the fixed bed reactor at 700°C and a residence time of 10 min. On the other hand, the volatile matter content in DAF-S2 char was 14.5 wt. % and this suggests that decomposition of DAF-S2 was not accomplished at 700°C and a fraction of organic matter was still un-released from the solid matrix. This observation is in line with results obtained from TGA pyrolysis which show a significant mass reduction at 750°C, higher temperature than the laboratory scale pyrolysis tests were performed (see Fig. 1 and 2). With respect to nitrogen only 9 -12 % of the initial N content in the sludge samples were retained in the pyrolysis char, thus it is concluded that the majority of the nitrogen was released in form of gaseous components or was retained in the oil/water fraction.

The results of the gas analysis for DAF Sludge 2 are presented in Fig. 5. The pyrolysis gas contained substantial amounts of combustible gases including methane (CH<sub>4</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>) and carbon monoxide (CO). The fraction of CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> was significant, above 20 vol. %, while a lower content of C<sub>2</sub>H<sub>6</sub> was observed, slightly above 5 vol. %. The fraction of CO was about 5 vol. % for most of the pyrolysis process but increased to 35 vol. % towards the end of the test while the content of other combustible gases (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>) declined. This suggests that CO may be the main gaseous compound released during the decomposition of the remaining volatile matter at higher pyrolysis temperatures. There was some nitrogen (N<sub>2</sub>) and oxygen (O<sub>2</sub>) present in the gas samples collected during pyrolysis because the reactor tube contained air at the start of the experiment. However, the fraction of N<sub>2</sub> and O<sub>2</sub> declined significantly when the apparatus was filled with pyrolysis gas.

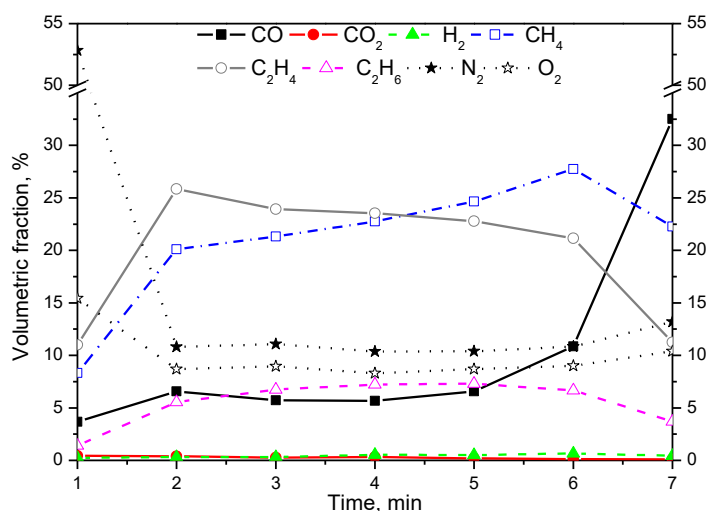


Fig. 5. Gas composition as a function of pyrolysis progress for DAF Sludge 2 at 700°C.

The average gas composition for all tested sludge samples is presented in Table 7. The standard deviation, related to the individual gas components, is relatively high because the gas composition varies over the duration of the pyrolysis process (see Fig. 5). The heating value of the product gas was calculated excluding the gas sample collected at the very beginning of the tests (1 minute in Fig. 5), since the combined volume of nitrogen and oxygen in it was about 70 % and the sample did not represent the composition of the product gas well. The heating values of the product gases from all sludges tested are relatively high at 16 - 27 MJ/m<sup>3</sup>. There are differences in the gas composition between the three feedstock. The concentration of H<sub>2</sub> is high for Sludge 1 and DAF S3 while very little H<sub>2</sub> was observed for DAF S-2. CO<sub>2</sub> is one of the gaseous components released during thermal decomposition of proteins, e.g. casein [12]. Since Sludge 1 and DAF S3 contain more protein, the content of CO<sub>2</sub> in the pyrolysis gas is also higher than for DAF S2. The concentration of ammonia and other N containing gaseous species were not measured in this study, however from the mass balance it can be concluded that about 90 % of all sludge N was released most likely in the form of NH<sub>3</sub>, HNCO or HCN [12-14] or retained in liquid pyrolysis products.

Table 7. Pyrolysis gas composition.

Gas, vol. %	Sludge 1	DAF Sludge 2	DAF Sludge 3
CO	9.8 +/- 2.7	11.3 +/- 9.6	9.3 +/- 1.7
CO <sub>2</sub>	27.7 +/- 6.7	0.23 +/- 0.1	12.1 +/- 3.2
H <sub>2</sub>	8.6 +/- 5.7	0.47 +/- 0.1	15.7 +/- 7.0
CH <sub>4</sub>	16.7 +/- 4.5	23.7 +/- 2.5	18.1 +/- 2.1
C <sub>2</sub> H <sub>4</sub>	9.3 +/- 0.9	21.4 +/- 6.4	14.9 +/- 2.4
C <sub>2</sub> H <sub>6</sub>	4.2 +/- 1.1	6.2 +/- 1.3	5.8 +/- 0.7
N <sub>2</sub>	3.7 +/- 1.8	11.1 +/- 0.9	6.7 +/- 4.7
O <sub>2</sub>	1.3 +/- 0.8	9.01 +/- 0.7	1.9 +/- 1.4
LHV, MJ/m <sup>3</sup>	16.36 +/- 1.9	26.47 +/- 2.4	21.96 +/- 1.8

### 3.4 Energy balance for pyrolysis products

The information obtained from the fixed bed pyrolysis tests was used for the energy flow analysis – an indicative energy balance for the pyrolysis products (Table 8). The energy entering with the residue was calculated for 1kg of dried residue, while the energy flows of the exit streams (char and gas) were evaluated on the basis of the lower heating value of the products and the mass balance of the pyrolysis process. The energy content in liquid product was calculated by the difference between the energy content in the feedstock and the solid and gaseous products. The energy balances should be viewed as qualitative due to the uncertainties in the determination of the absolute mass of the liquid and gaseous fraction. Nevertheless, it is considered as sufficiently accurate for the particular purpose of this research project, which is to select sludge appropriate for pilot scale pyrolysis tests.

Table 8. Energy content of each input and output streams for pyrolysis experiments at 700°C in a fixed bed laboratory reactor for dried dairy sludge samples.

Residue type	Input	Outputs		
	Sludge, MJ, %	Char, MJ, %	Gas, MJ, %	Oil, MJ, %
Sludge 1	17.25 (100)	2.50 (14.5)	8.88 (51.5)	5.86 (34.0)
DAF-Sludge 2	18.97 (100)	1.01 (5.3)	17.57 (92.6)	2.00 (0.39)
DAF-Sludge 3	25.49 (100)	1.71 (6.7)	16.31 (64.0)	7.46 (29.3)

The vast majority (92 %) of the initial energy content of the dried DAF-Sludge 2 is preserved in the pyrolysis gas. Because the volatile matter content in DAF-S2 char (see Table 4) is still relatively high after the fixed bed pyrolysis a slightly higher carbon conversion into gaseous products is anticipated for pilot scale tests since mixing at a larger scale will enhance heat and mass transfer processes compared to the laboratory scale process.



Over 60 % of the initial energy content of the dried DAF-Sludge 3 is retained in the pyrolysis gas. There is still a significant amount of energy (29.3 %) retained in the liquid product from pyrolysis of this sludge. However, the distribution of pyrolysis products may change in a pilot scale operation where a rotary drum reactor is used. A reduced liquid product fraction can be expected since the residence time of the vapours will be longer as opposed to lab scale where the vapours were cooled down immediately after release from the solid residue structure. Oils and tars may be cracked to liberate gases like CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> as well as oxygenated species.

On the other hand, only about 50 % of the initial energy content of the dried Sludge 1 was conserved in the pyrolysis gas and a substantial amount of the energy was retained in the oil (31.9 %) and the char (14.5 %). Therefore, it is suggested that this residue is unsuitable for recovery of energy in the form of a high calorific value gas.

Yet, based on the preliminary results from the laboratory fixed bed pyrolysis and qualitative energy balance it can be concluded that most of the energy from the dried sludge samples was retained in the form of pyrolysis gas for the DAF sludge.

### 3.5 Seasonal variability in sludge properties

In the course of this study we tested three samples of DAF Sludge 2 and two samples DAF Sludge 3 collected on different dates in order to investigate the effect of seasonal changes on the properties of sludge and distribution of pyrolysis products.

Table 9 Properties of different of dried dairy sludge collected on different dates.

Properties, wt. %	DAF S2 November 2015	DAF S2 May 2016	DAF S2 October 2016	DAF S3 March 2016	DAF S3 December 2016
Moisture, ar.	60.26	71.2	67.60	94.54	92.10
Moisture, after bench drying	18.32	5.05	6.24	8.93	12.41
Ash content, db.	31.89	26.32	36.41	19.00	6.58
Volatile matter, db.	-	73.33	61.89	77.46	80.59
Fixed carbon, db.	-	0.35	1.70	3.54	12.83
LHV, MJ/kg db.	18.105	21.760	18.966	25.487	19.463
C, db.	46.89	50.22	43.31	54.90	45.78
H, db.	6.41	7.84	6.94	8.71	6.25
N, db.	1.24	1.32	1.63	2.37	15.11
S, db.	0.20	0.15	0.11	0.40	0.87
O, db.	13.37	14.15	11.60	14.62	25.31

The DTG profiles obtained during the programmed heating experiment for the dried DAF-S2 samples in an inert atmosphere is presented in Fig. 6. There was a considerable difference in the DTG curves for DAF-S2 collected in November, May and October. The difference arises from the fact that different milk products were produced on these dates and the composition of the effluent and resultant sludge samples were different. In November 2015 the factory produced casein and whey powders; in May 2016 butter, skim milk powder, whey powders and casein while in October 2016 skim milk powder was produced in very small quantities. The different DAF-S2 samples have quite similar net calorific values in the range from 18.1 to 21.7 MJ/kg while volatile matter content was the highest at 73.3wt. %, the ash content was the lowest at 26.3 wt. % for the sludge sample from May. The mass balance of the pyrolysis products of the three DAF S2 samples was also slightly different. The fraction of the liquid products was the highest for the November 2015 sludge sample.

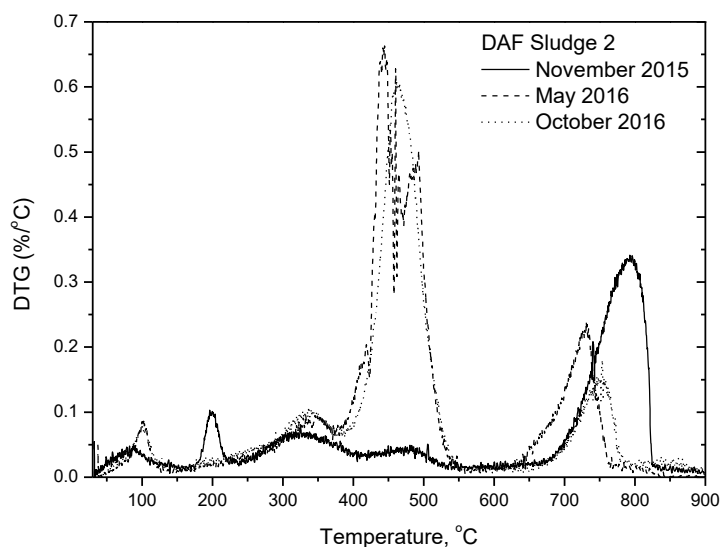


Fig 6. DTG curves for dried dairy sludge samples from Company 2 collected on different dates.

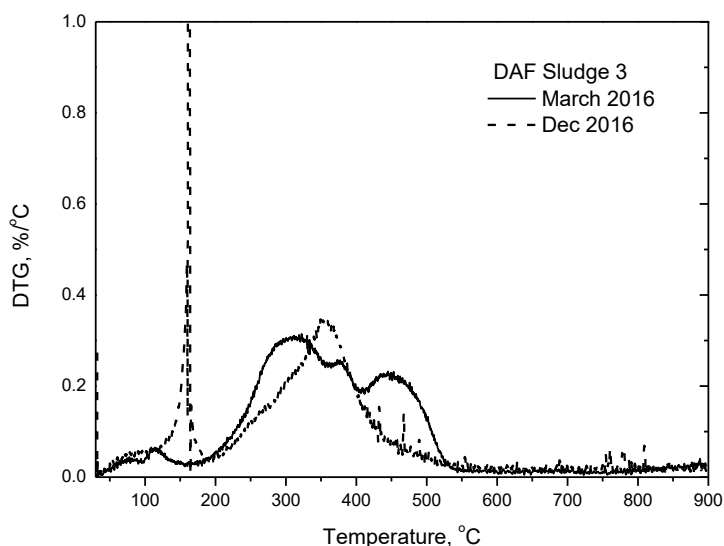


Fig 7. DTG curves for dried dairy sludge samples from Company 3 collected on different dates.

There is a significant difference in the DTG curves for DAF Sludge 3 collected in March and December 2016 (see Fig. 7). The difference arises from the fact that different milk products were produced on these dates and the composition of the effluent and resultant sludge samples were different. In March the factory produced butter, skim milk powder, sweet whey powders, casein and cheese while in December casein was not produced. DAF S3 collected in December has a lower net calorific value (19.5 vs. 25.5MJ/kg), much lower ash content (6.58 vs. 19 wt. %), a similar volatile matter but higher fixed carbon content (12.8 vs 3.5 wt. %) and very high nitrogen (15 vs. 2.4 wt. %) and oxygen contents (25.3 vs. 14.6 wt. %) (see Table 9). The mass balance of the pyrolysis products of the two DAF samples is also very different (see Fig 8). The main pyrolysis product for the December sample is liquid, 44 wt. %, while gas accounts for less than 40 wt. %.

There is need for a systematic study regarding the relation between dairy company's product portfolios, waste water treatment technology used and the properties of the resultant sludge.

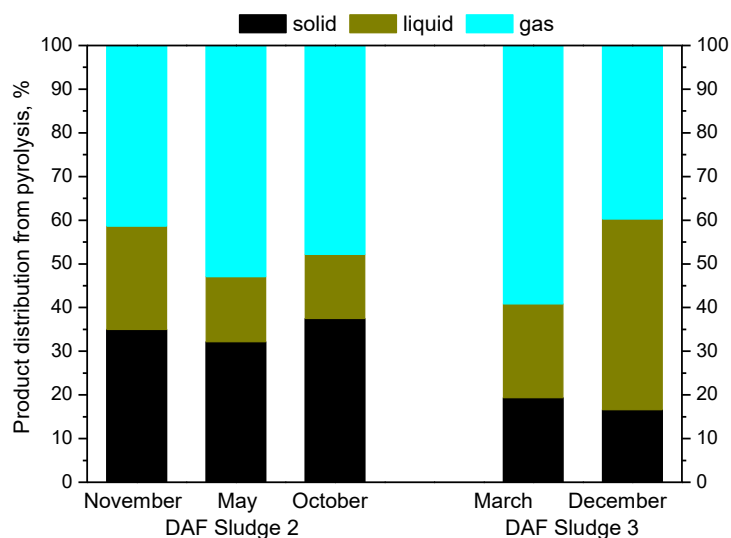


Fig. 8 Mass balance for pyrolysis products of DAF Sludge 2 and DAF Sludge 3 collected on different dates. Pyrolysis in a fixed bed reactor at 700°C for 10 min.

#### 4. Conclusions

Samples of two different types of dried sludge from wastewater treatment of milk processing plants were pyrolysed in a fixed bed laboratory reactor and analysed using TGA. Pyrolysis of dried dairy sludge containing fat and grease, DAF sludge 2 and DAF Sludge 3, produced gases with higher calorific values (26 and 22 MJ/m<sup>3</sup>) than the biological sludge – Sludge 1 (16 MJ/m<sup>3</sup>). The results obtained from qualitative energy balances show that the vast majority of the initial energy content of the dried DAF Sludge 2 was retained in the pyrolysis gas. Hence, it is concluded that this sludge residue is suitable for recovering energy in the form of a high calorific value gas and was selected as an appropriate feedstock for pilot scale pyrolysis tests. There is need for a systematic study regarding the relation between dairy companies' product portfolios, the waste water treatment technology used and the properties of the resultant sludges. Furthermore, seasonal change in sludge composition and its effect on the distribution of the pyrolysis products needs to be studied in a more systematic way.

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