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By-products of fish-oil refinery as potential substrates for biogas production in Norway: A preliminary study

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ABSTRACT

Norway is one of the biggest fish exporters in the world, and the fish industry is the second biggest economy of the country after oil and natural gas. As fish industries expand rapidly, the resulting fish-oil refining by-products are also receiving an upsurge interest, giving an enormous window of opportunity in generating bioenergy through this route. A number of fish-oil refinery by-products such as soapstock, glycerol, ethyl monoesters (light and dark) were utilized in the present study where the anaerobic digestion feasibility of these by-products as co-substrates with fish ensilage (acidified fish waste) was investigated. The method utilized was biomethane potential experiment by employing a series of 0.5 L batch bottles as anaerobic digesters operated at total feeding of about 7.0 g with co-substrates feeding ranging between 0.6 and 2.0 g per bottle. The digestion environment was set at extreme mesophilic having temperature of 39 ± 1 °C. During the ~65 days of experiment, it was found that accumulated volumetric biogas yield (in mL) from co-digestion of monoesters and fish ensilage was much higher than that of the mono digester operated with fish ensilage alone. The accumulated yield from light and dark monoesters co-digesters amounted to ~2100 mL and ~1950 mL respectively. In terms of specific biogas yield, highest yield was obtained from the soapstock co-digesters with an average peaking to 775 mL/gTS. The average methane content in biogas for all the digesters over the course of the experiment was found as ca 61%. The study concludes that fish-oil refinery by-products as co-substrates with fish ensilage upon utilization to anaerobic digestion plants can potentially offer Norwegian fish refineries an excellent opportunity to contribute heavily in local bioeconomy.

1. Introduction

Fish is a vital source of animal protein for human consumption. Globally, per capita food fish consumption has grown from 9.0 kg in 1961 to 20.2 kg in 2015, at an average rate of about 1.5% per year [1]. Together with increased fish consumption, annual fish production also increases. According to food and agriculture organization of United States (FAO), worldwide total fish harvest resulting in from capture and aquaculture reached to 171 million tonnes in 2016, out of which 88% was used as human consumption and the remaining 12% as non-food purposes [1]. In order to enable human consumption, raw fish in a typical production application is processed by using various techniques resulting in considerable edible and non-edible fraction of wastes (also called as rest raw materials) such as heads, viscera, bones, eggs, blood and scales [2]. These wastes account approximately 27% of the total fish landed from harvest [1]. Also, fish sludge [3] resulting in largely from uneaten fish feed and fish waste (category 2 waste) resulting in from dead or slaughtered fish (enforced due to sickness) consist of a large portion of waste within aquaculture fishing. Considerable part of these waste streams, although having high nutritive value for human consumption, are still under-utilized or disposed of either for landfills or incineration causing environmental problems including ground water pollution and toxic gas emissions.

In order to reduce environmental impact of wastes generating from a various sources, a number of approaches were utilized, where using wastes as fillers or co-raw-materials for different production chains are reported [4,5]. Moreover, wastes as sole material for subsequent treatment to energy production are also demonstrated in many applications. As fish waste is rich in proteins, fats and organic constituents, it can characteristically suit to biological conversion through anaerobic digestion for producing biogas (CH_4, CO_2, H_2S, and trace gases). Anaerobic digestion is an anoxic, controlled temperature microbiological degradation process, which transforms organic wastes and substrates from various sources and origins to renewable biogas and digestate slurry readily useable as fertilizer to cultivable lands. Consequently, a sustainable utilization of wastes contributing to closing the loop of traditional

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linear bioeconomy through this route can be achieved.

Being the country's second biggest economy, Norway produced approximately 2.4 million tonnes of fish in 2017 primarily through aquaculture fishing, which consists 1.7% of the world's total production [6]. Although a big market, the fish industries in Norway likewise world's fishing business encounter a substantial fish waste generation from leftovers of cut fish and fish sludge waste including fish feces and surplus fish feed resulting in from fish farms.

Likewise fish itself, rest raw materials are highly nutritive and contain valuable minerals, vitamins and lipid fractions which have a great potential to benefit human beings overall health [7]. Therefore, rest raw materials should not be treated as waste or less valuable than the main product. Considering the offered benefits, the rest raw materials of fish waste can potentially be utilized for a wide range of purposes including production of fish-oil, fish cakes, chemicals, bioactive and pharmaceutical components and other components for human consumption and even for biofuel production [8–10].

Fish-oil deriving from rest raw materials can further be refined to remove undesirable components without losing nutritionally valuable long chain polyunsaturated fatty acids (PUFA) and thus enables to extract omega-3 oil [11]. The omega 3 oil refining process involves multiple production steps generating by-products of various proportions besides the main product omega 3 oil. These by-products although cannot be directly used for human consumption, due to their organic chemical contents favor various fuel or energy applications.

For example, ethyl monoesters (including light and dark), as by-products, have the diesel like properties, which make them suitable for combustion application to generate heat that subsequently meets partial energy requirement of a fish-oil refining plant. Although combustion of esters in comparison to fossil diesel is superior in emission properties [12], esters as biofuels are not directly compatible in terms of viscosity and miscibility in the existing applications [13,14], and hence they have not been considered for commercial application yet. Esters can however become a good candidate for anaerobic digestion to biogas production. A previous study [14] reported that using some certain ester compounds with a certain concentration (up to 5 g/L) can contribute to improve biogas production from anaerobic digestion.

Another by-product, soapstock (SS), has the potential to produce biogas, and its viability for liquid fuel production was also suggested [15]. Soapstock originating from edible oil manufacture has been studied for biodiesel production including biogas [16] and value added chemicals [17]. Also, it has been reported [16] that by co-digesting soapstok with grass, cattle manure and fruit and vegetable waste, biogas yield between 770 L/kgVS and 800 L/kgVS can be obtained.

Spent bleaching earth (SBE) as a by-product from fish-oil refinery has not been well explored for energy production, but similar product generating from vegetable oil refining plant, also called as SBE or spent bleaching clay has long been utilized in biogas plants [18], and its potential to biodiesel production by enzymatically extracting lipases was mentioned. Besides biogas and biodiesel production, SBE was also utilized for other alternative applications, for instance, for dehumidification of air [19]. A recent study [20] on fish-oil refinery SBE reported that by adding 10% w/w of bleaching earth with cattle manure the increase in 163% biogas yield over 102 days period of anaerobic co-digestion can be obtained.

By-product alkaline fish glycerine (AFG) has the characteristics suited to many applications including production of plastic, food and drugs, lubricants and hydrogen [21] or as feedstock for anaerobic digestion to biogas [22]. Guðmundsson et al. [20] utilized fish-oil refinery AFG for biogas production and found that by using 3% w/w AFG in combination with cattle manure can result in 188% increase in biogas yield with maximum specific yield of 704 mL/gVS.

Even though the resulting waste streams from fish-oil refinery have an enormous potential in producing biogas, only a handful amount of past studies treated one or two of these streams in a single study context. The present work, nevertheless, utilized multiple by-products streams: alkaline fish glycerine, soapstock, mono and dark ethyl esters, and further compared their biogas potential performance with the conventional fish ensilage, enabling a more realistic assessment of their energy production impact as AD substrates. As the fish waste anaerobic digestion alone is inherently difficult because of various processing challenges [23], the co-digestion of fish waste with fish-oil refinery by-products can emerge as an alternative solution to overcome the fish waste's utilization drawbacks. Moreover, as for general benefits, the co-digestion approach is likely to result in numerous processing advantages ranging from C:N ratio optimization, macronutrients balance to methane production enhancement [24]. Besides, as the work emphasizes on examining the feasibility of local Norwegian feedstocks, the obtained results are expected to provide valuable information to the local Norwegian fish farms in increasing their involvement in sustainable bioenergy advancement. Such results are also likely to pave the way for AD of fish-oil refinery by-products to proliferate in compatible scenarios within the global context.

2. Materials and methods

2.1. Feedstocks

The feedstocks used for the study were inoculum and substrates from fish farm and fish-oil refinery as discussed in the sub-sections below.

2.1.1. Inoculum

For anaerobic digestion start-up, inoculum is needed. The anaerobic digestion sludge from Ecopro biogas plant, located nearby Trondheim (coordinate: 63.75° N, 11.92° E) was used as inoculum. The Ecopro plant operates with organic waste as the main feedstock at digester temperature of about 39 °C, which was utilized in the present experiment. The inoculum after collection was degassed by incubating at the original temperature for over 30 days prior to experiment, allowing the depletion of residual biodegradable content [25], and hence became ready for experimental usage.

2.1.2. Substrates

Ensilaged fish waste and four different residues resulting in from fish-oil refining process were used as feedstocks. The residues include soapstock (SS), alkaline fish glycerin (AFG), light ethyl monoester (LME) and dark ethyl monoester (DME). The origins of different residues during fish refining process is depicted in Fig. 1 and their physical and chemical properties are summarized in Table 1, which also includes properties of inoculum during start-up. Substrates utilized for experiments were provided by Mr. Terje Hyldmo from Biokraft AS, Trondheim, Norway.

2.2. Biomethane potential test

The biological methane potential (BMP) tests were performed according to the protocol ISO 11734 (1995), as described by Møller et al. [26]. Principally, the test involves degradation of a definite amount of substrate at a constant digestion temperature over a given period of time, typically between 30 and 90 days. This substrate amount for a given substrate type is usually kept different between the two experimental reactors so that an organic loading rate (gram input per liter of digester volume) per reactor can be differed. The organic loading for an individual BMP reactor is typically expressed by a term called substrate to inoculum ratio (S:I) based on which the daily biogas evolution profile in terms of speed, productivity and specific yield are interpreted, and further compared between the reactors. The experimental design used for biomethane potential test is detailed in the sub-section below.

2.2.1. Experimental set-up and reactor specifications

The design parameters utilized for experimental set-up are given in Table 2. In order to set-up batch assays, approximately 200 g of degassed inoculum was combined with different amount of substrates (0.6–7.1 g)

across the 500 mL infusion bottle reactors (see Table 2). Afterwards, the bottles were sealed with butyl rubber stoppers and aluminium caps. The assays were prepared in duplicate having an approximate S:I of 0.25, calculated based on the total solid (TS) content of inoculum and substrates (FE, SS and AFG). TS based input parameters of the reactors are also included in Table 2. Worthwhile to note that LME and DME contain little or no solid, and hence no data on TS analysis for these substrates were reported in Table 2.

In addition to the experimental bottles containing both inoculum and substrates, two bottles as blanks (reactor C1 and C2) were run with inoculum only (see Table 2). During start up, the batch bottles after feeding and sealing were flushed with pure N_2 for 5–10 min to ensure anaerobic condition. Afterwards, the assays kept heated in an incubator (Termaks AS, Norway) for about 70 days at temperature of 39 ± 1 °C. The reactors were manually stirred 2–3 times daily and the produced biogas on the headspace was periodically measured by passing through a water displacement column, similar to the one described elsewhere by [27]. The actual biogas data was recalculated for standard temperature and pressure (STP) applying combined gas law [28] and compared against the theoretical methane yield (m^3/kgVS) using equation (1) below [29].

$$B_{O,th} = \frac{0.415\ Carbohydrates + 0.496\ Proteins + 1.014\ Lipids + 0.373\ Acetate + 0.530\ Propionate}{(Carbohydrates + Proteins + Lipids + Acetate + Propionate)} \quad (1)$$

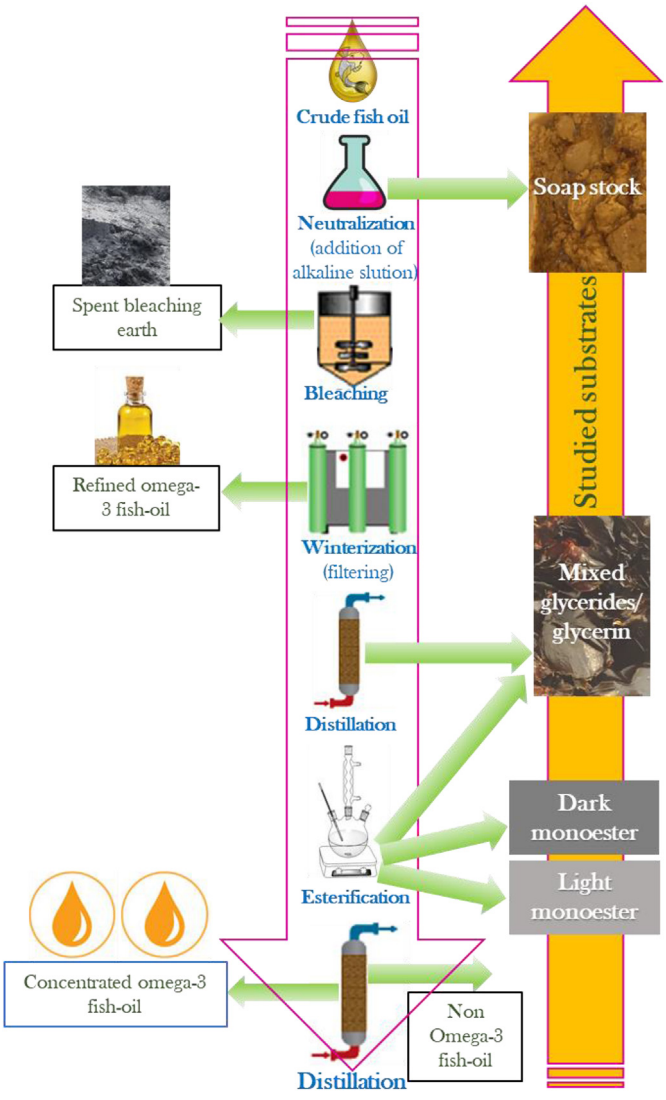

Fig. 1. A typical process flowchart of fish-oil refining to omega-3 oil.

2.3. Analyses

Physical properties such as dry matter, volatile solids and pH of substrates, inoculum and digestate were measured by employing available *in-situ* facilities, while some other properties such as the amount of carbohydrate, lipid, Kjeldahl nitrogen, fat and protein were evaluated by the external lab, Eurofins AS (Trondheim, Norway).

Dry matter and volatile solids were analyzed according to the protocol APHA (American Public Health Association, 2005), described elsewhere by [30,31]. For dry matter (total solid, TS) analysis, sample was heated for continuous 24 h to 105 °C using an oven (Termaks AS, Norway). The dried sample amount was then compared against the wet sample following the equation (2) below to calculate the total solid content in percent.

$$\%TS = \frac{Dried\ \ sample\ \ weight - Tray\ \ weight}{Wet\ \ sample\ \ weight - Tray\ \ weight} \quad (2)$$

Volatile solids were determined by incorporating difference between the TS and the sample ash content. In order to convert sample into ash, the dried sample was combusted for about 3 h at 550°, using a muffle furnace (Nabertherm, Germany). The ash amount together with the TS content was then used in equation (3) to determine VS content in percent.

$$\%VS = \frac{Combusted\ \ sample\ \ weight - Tray\ \ weight}{Dried\ \ sample\ \ weight - Tray\ \ weight} \quad (3)$$

For pH measurement, litmus pH strips were used.

In order to evaluate the gas composition, gas was routinely sampled and analyzed by a gas chromatograph (SRI 8610C, SRI Instruments, USA). The two columns (2 m Molecular sieve 13x and 2 m Silica gel) of the GC were configured for H_2, CO_2 and CH_4 measurement to characterize biogas in terms of these three components. The gas was sampled in a 10 mL sealed infusion bottle and saved in a refrigerator (maximum one week holding) at ca 4 °C before utilizing for GC analysis. In addition to gas measurement, the GC was also used for liquid VFA analysis. This, however, was possible only once during the course of the experiment because of technical issues resulted in by GC column damage.

Table 1
Selected physical and chemical properties of studied substrates.

Properties	FE	SS	AFG	LME	DME	Inoculum
Total solids (TS), %	30.63	32.50	55.30	N.D.	N.D.	4.43
Volatile solids (VS), %	28.95	N.D.	N.D.	N.D.	N.D.	3.22
[a]Carbohydrates, %	12.00	N.D.	N.D.	N.D.	N.D.	5.30
[a]Proteins, %	10.30	N.D.	N.D.	N.D.	N.D.	1.56
[a]Fats, %	51.00	21.1	N.D.	N.D.	N.D.	24.60
[a]NH_4–N, g/kg	1.20	N.D.	N.D.	N.D.	N.D.	0.61
pH	3.90a	8–9[b]	6–7[b]	6–7[b]	6–7[b]	7.90a
[a]Chemical oxygen demand (COD), g/L	429.00	N.D.	N.D.	N.D.	N.D.	N.D.
[a]Lower heating value (LHV), MJ/kg	13.00	N.D.	N.D.	N.D.	N.D.	1.60

[a] Measured by Eurofins AS.
[b] Measured by pH strips.

Table 2
Designed parameters utilized for experimental set-up.

Batch anaerobic digestion experimental set-up parameters[a]													
Experimental reactor	Substrate input												
	Inoculum		FE		SS		GLY		LME		DME		S:I input
	weight, g	*TS, g*	*weight, g*	*TS, g*	*weight, g*	*TS, g*	*weight, g*	*TS, g*	*weight, g*	*TS, g*	*weight, g*	*TS, g*	
C1	200	8.86	.	.	.	.	.	.	.				0
C2	200	8.86	.	.	.	.	.	.	.				0
FE1	199.8	8.85	7.1	2.21									0.25
FE2	200.0	8.85	7.0	2.21									0.25
FE + SS1	200.3	8.87	5.2	1.59	2.0	0.65							0.25
FE + SS2	200.3	8.87	5.2	1.59	1.9	0.62							0.25
FE + GLY1	201.5	8.93	6.6	2.02			0.40	0.22					0.25
FE + GLY2	200.1	8.91	6.7	2.05			0.35	0.19					0.25
FE + LME1	201.5	8.93	6.0	1.84					1.00	0.43			0.25
FE + LME2	202.8	8.98	6.0	1.84					0.90	0.39			0.25
FE + DME1	200.7	8.89	6.4	1.96							0.60	0.27	0.25
FE + DME2	200.3	8.87	6.5	1.99							0.60	0.27	0.25

[a] Data presented in this table were rounded-off to the nearest whole numbers.

2.4. Energy yield

The total energy yield from the volumetric biogas yield (mL/g substrate) was calculated by multiplying the total biogas production (m^3/Ton, wet basis) with the lower heating value of methane of 35.89 kJ [32] and the factor 0.60 for 60% v/v methane in the biogas.

2.5. Kinetic modeling

In order to evaluate anaerobic digestion efficiency, kinetic analysis was performed. Two kinetic analysis models first-order and modified Gompertz model, shown by equations (4) and (5) respectively, were used:

$$G(t) = G_0 \times \left\{1 - e^{(-Kt)}\right\} \tag{4}$$

$$G(t) = G_0.\exp\left\{ - \exp\left[\frac{R_{max}.e}{G_0}(\lambda - t) + 1\right]\right\} \tag{5}$$

where.

G(t): the cumulative methane yield at a digestion time t days (mL/gVS_{added});
G_0: the methane potential of the substrate (mL/gVS_{added});
K: the biogas production rate constant (first-order disintegration rate constant) (1/day);
t: time (days);
R_{max}: maximum methane production rate (mL/gVS_{added});
e: exp (1) = 2.7183;
λ: lag phase (day).

The kinetic parameter values obtained from the modified Gompertz model were optimized for R_{max} and λ using Microsoft Excel solver tool.

3. Results and discussions

3.1. Feedstock characterization

The characterization results of inoculum, FE, SS, AFG, LME and DME are given in Table 1.

It can be seen that all the analyzed materials except inoculum contain a high dry matter content, which ranges between 31% and 55%. Of these, AFG dry matter content was found to be the highest (55.30%). AFG is a by-product resulted in from the distillation and esterification steps of fish refining process. Distillation separates AFG as a residual product which forms to solid at room temperature environment [33]. This allows a substantial amount of moisture to evaporate, and as a result, the proportional distribution of organic and biodegradable components to increase, raising the dry matter content.

Unlike AFG, the TS content of SS and FE was found pretty similar, kept at around 30%, which is in good agreement with the past studies [23,34] for similar substrates. Technically, substrate TS content exceeding 30% of the total weight may influence AD negatively, especially, in terms of hydrolysis and liquid to gas mass transfer rate [35]. However, by careful utilization of feedstock and process design such as gradual feedstock loading, combined meso and thermophilic reactors and co-digestion seem to address many problems associated with high TS feedstock AD [36].

In addition to TS, fat and protein content was also measured, and the results obtained from an external laboratory for FE are reported in Table 1. Contrary to the basic animal wastes (i.e., cattle manure, pig manure.), fish wastes in general contain higher amount of lipid and fat, which was also confirmed in the present analysis being measured as 51% and 10.3% respectively. As known, among the different components that a feedstock consists of, lipid (or fat) gives the highest biogas yield potential [24]. Therefore, a substrate with a higher lipid content is likely to produce more biogas. However, in practical AD applications, elevated lipid or fat content substrate may trigger various process instabilities associated with imbalance in the production of ammonia and sulphide, low biogas yield and further to inhibition of methanogenesis [37]. Several approaches have been employed in order to circumvent issues arising due to lipid rich substrate loading. Of these, co-digestion is considered widely and also used in the present study.

As for pH, AFG, DME and LME exhibit similar values ranging between 6 and 7, while FE and SS show contrasting values with FE being 3.9 and SS being ~9 respectively. Since SS was released from alkalinization step of fish-oil refining (Fig. 1), it's pH as compared to the other substrates was logically found to be the highest, i.e., ~9. However, in order to enable this substrate suitable for AD, the pH was adjusted to ca 7.0 by adding sodium bicarbonate. Similar to SS, the high acid content of FE does not suit direct application to AD, as this may result in mismatch of acetogensis and methanogenesis and consequently to drop, or in worst case, to inhibit methane yield. Hence, pH of FE prior to incubation was adjusted to ~7.0 by means of sodium bicarbonate addition, serving as pH buffer.

3.2. Anaerobic digestion experiment

In order to evaluate biomethane potential of studied substrates, anaerobic digestion using batch digesters was conducted and the obtained results are presented in this section. The biogas production values are expressed both in terms of volume basis, where the daily volumetric

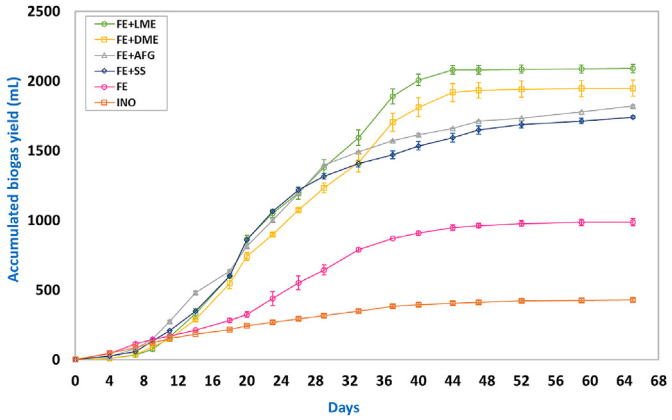

Fig. 2. Accumulated biogas yield from all reactors.

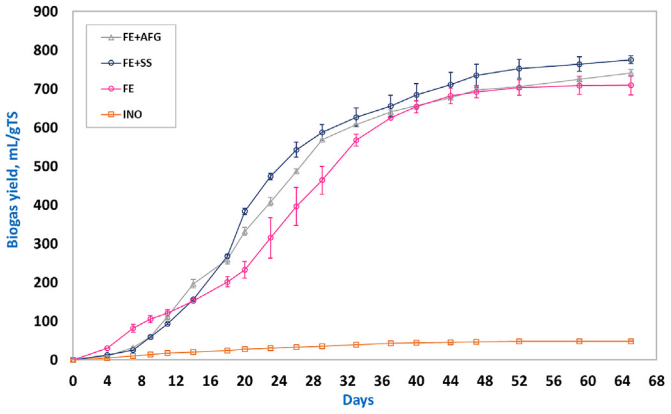

Fig. 3. Specific biogas yields from the reactors INO, FE, FE + AFG and FE + SS.

biogas yield per gram substrate input (mL/d) are given, and weight basis, where the daily volumetric biogas yield per gram TS input (mL/gTS) are given. Biogas yields resulting in from co-digestion of FE with DME and LME are only reported on volume basis.

Fig. 2 shows the accumulated biogas yields from the co-digestion reactors: FE + SS, FE + AFG, FW + DME, FE + LME, and mono-digestion reactors: FE and INO. INO reactor operated solely with inoculum as feedstock, which served as control, while FE reactor was run on fish ensilage as feedstock, acted as reference for co-digestion reactors.

As seen, after 65 days of digestion, volumetric biogas yields from co-digesters FE + LME and FE + DME reached to total 2089 mL and 1948 mL respectively. Reactors FE + AFG and FE + SS produced almost equal amount of biogas, totalled to ca 1800 mL. Compared to accumulated biogas yield from FE alone, which reached to ca 986 mL, co-digestion reactor FE + LME and FE + DME produced roughly 2 times more biogas, and the other two digesters FE + SS and FE + AFG produced almost 1.8 times more biogas. In terms of energy yield, this extra biogas yield from the co-digesters can potentially contribute to additional ~1075 kWh/ton of maximum energy from FE + LME, followed by ~900 kWh/ton from FE + DME, ~800 kWh/ton from FE + AFG and the minimum ~680 kWh/ton from the reactor FE + SS respectively (Table 3). Assuming no net CO_2 emission from AD processing, the estimated maximum energy yield (ca 2000 kWh/ton, Table 3) from FE + LME corresponds to the maximum reduction of 0.826 ton CO_2/ton feedstock emission, which would otherwise have been released from fossil fuel plants. Given the net rise of CO_2 emission from the Norwegian fisheries in the last years, the utilization of fish-oil refinery by-products for biogas production can offer a promising alternative to partially address the current carbon footprint as well to meet the Norwegian's national goal of reducing 40% CO_2 emission by 2030.

On the other hand, comparing the specific biogas yield among the FE, FE + AFG and FE + SS reactors in terms of per kg TS input, similar pattern of cumulative yield was observed (Fig. 3), where the total yield of these reactors after 65 days of digestion reached to ca 710 mL/gTS, 745 mL/gTS and 775 mL/gTS respectively. Guðmundsson et al. [20] found the similar specific yield for co-digestion of 1.5% of AFG with cattle manure. However, in their study as the AFG concentration increased, the biogas yield was found to drop sharply. Observing the specific yields among the digesters again, the net gain in biogas yield (per kg TS input) resulting in from the addition of fish refinery by-products was found to maximize to only 65 mL/gTS from FE + SS corresponding to energy increase of ca 431.2 kWh/Ton TS. This implies that the benefit obtained in terms of energy yield due to the co-digestion is much less for specific biogas yield as compared to the volumetric yield (described above). The reason for this might be associated with the process instability caused by the development of ammonia or pH, which, however, could not be confirmed, as no measurement of these was possible to carry out during the course of experiment. Also, as the study did not investigate the effect of variable feed input on biogas potential, the optimal specific biogas yield for any particular by-product cannot be suggested.

In addition to the biogas yield, the methane content in biogas from all the digesters at a routine interval (mostly once in a week) was performed. As observed (Table 5), the methane content kept fairly stable among the digesters in different phases of the experiment. Not surprisingly, methane content between week 1 and 3 was less than 60% v/v for all the reactors due to the development of lag phase and the extent of hydrolysis. From week 4 until week 7, the methane content developed quite substantially maximizing to 75% v/v from reactor FE + LME1. On an average, the methane content for all the reactors in this period hit to over 67% v/v which stabilized at around 65% v/v between week 8 and 9. The rise in methane content in the middle phase of the experiment was associated with the increased methanogenesis which gradually stabilized to a lower value at the back end of the process due to the reduced feedstock availability. Solli et al. [23] found the similar methane content range in their continuous reactor experiment run on fish ensilage. Moreover, this average methane content between 60 and 70% v/v is prevalent in existing commercial biogas plants, which indicates the viability of present results in practical approaches.

Table 3
Estimated energy yield of biogas produced from studied substrates.

Reactor	Total feed input [g]	FE input [g]	Co-substrate input [g]	Total biogas [mL]	Energy[a] [kWh/Ton]	Energy yield increase [kWh/Ton]
FE	7.10			985	920.27	
FE + SS	7.20	5.20	2.00	1738	1601.23	680.96
FE + AFG	7.03	5.00	2.03	1818	1715.43	795.17
FE + LME	6.95	5.00	1.95	2089	1993.83	1073.57
FE + DME	7.10	5.10	2.00	1948	1819.98	899.71

[a] Assuming 60% v/v of biogas is methane.

3.3. Kinetic modeling analysis

As mentioned, the first-order and modified Gompertz kinetic models are employed for predicting biogas yields from the studied substrates. The kinetic parameters of the models (i.e., k, λ and R_{max}) were determined using nonlinear regression in Microsoft Excel. Furthermore, the predicted biogas yields were compared with the measured yields to evaluate the model that shows the best fit.

Table 4 summarizes the results of the kinetic analysis of experimental data produced by the reactors FE, FE + SS and FE + AFG. Furthermore, Fig. 4 shows biogas yield comparison between measurement and models.

Table 4
Comparison between the results obtained from the first order and the modified Gompertz model analysis.

Reactor	FE	FE + SS	FE + AFG
Measured biogas yield [mL/gTS]	709	775	741
First order kinetic model			
Kinetic constant, k [1/d]	0.0133	0.0061	0.0056
Predicted biogas yield [mL/gTS]	580	328	307
Accuracy: predicted vs. measured biogas yield [%]	82	42	41
Modified Gompertz model			
Predicted maximum biogas production rate, R_{max} [mL/gTS.d]	20.18	30.67	30.18
Measured maximum biogas production rate [mL/gTS.d]	17.20	20.88	19.60
Accuracy: predicted vs. measured R_{max} [%]	85.23	68.07	65.00
Lag phase, λ [d]	7.43	9.91	9.96
Predicted biogas yield [mL/gTS]	891	885	884
Accuracy, predicted vs. measured biogas yield [%]	80	86	81

As seen, by using first order kinetic model the biogas yields from the reactors FE, FE + SS and FE + AFG were calculated to be 580 mL/gTS, 328 mL/gTS and 307 mL/gTS respectively, which compared to the measured values were 18%, 58% and 59% lower. This means that the first order kinetic model was only able to predict biogas yield from the mono-digestion reactor (i.e., FE) with better accuracy as compared to the co-digestion reactors: FE + SS and FE + AFG. The reason for this maybe because of difference in hydrolysis rates between mono and co-digested substrates and inadequacy of first order kinetic model to predict hydrolysis caused by co-feeding [38]. Due to the addition of SS and AFG with FE, the total fat and protein concentration in the co-digesters became higher than the mono-digester FE, which ultimately tend to slow the hydrolysis rate. However, even though the slower hydrolysis, the co-digestion may improve substrate degradability in the successive steps by maintaining enhanced nutrient balance, and thus enabled to increase biogas yield.

Observing the results obtained from the modified Gompertz model, the lag phase between mono-digester (FE) and co-digesters (FE + SS and FE + AFG) was found to considerably vary with corresponding value of 7.43 days, 9.91 days and 9.96 days respectively. Lag phase implies the time requires before the start of biogas production and can be indicative that hydrolysis is the rate limiting step [39]. The longer lag phase time of FE + SS and FE + AFG might be associated with the longer conversion times resulting in from the increased concentration of proteins and fats in the input substrates. As the co-digesters had higher dosing of proteins and fats compared to the FE reactor, they are likely to be influenced by the limiting hydrolysis rate, indicated by the length of the lag phase.

In terms of biogas yields, the predicted values by the modified Gompertz model closely coincided with the experimental values with corresponding accuracy of 80%, 86% and 81% for the reactors FE, FE + SS and FF + AFG respectively. This suggests that the modified Gompertz model, compared to first order kinetics, was more efficient in predicting the final biogas yield of the studied substrates, especially for the co-digestors that utilize binary mixture of substrates. However, the biogas evolution profiles resulting in from Gompertz model seemed to be well-fit with those from the measured values until day 28 for co-digestors and day 44 for mono-digester, after which the difference between measured and modelled yields increased gradually. This might be attributed to the methanogenic metabolism influenced by the process parameters resulting in from the present set-up. For example, in this study the batch reactors were shaken manually, during which they were generally exposed to the room environment for a short period of time when there might be a slight drop in incubation temperature, and hence disrupted methanogens activity.

Likewise biogas yield, the maximum biogas production rate (mL/gTS.d) was also predicted fairly accurately by the modified Gompertz model. While the measured production rate corresponding to the digesters FE, FE + SS and FE + AFG were ca 17, 21 and 20 mL/gTS.d respectively, the predicted yields were 20, 31 and 30 mL/gTS.d respectively. The maximum production rate for the reactors evolved between days 29 and 33 with the earliest by the FE + SS and the latest by the FE. This can also be confirmed from the biogas yield data (Fig. 2) which shows a stable increase after week 5. Worthwhile to note that the methane content in biogas for the digesters also maximized around these days between week 5 and 6. However, the lower production rate in the actual case maybe ascribed by the process uncertainties caused by the VFA, pH, ammonia and methanogens population which, nevertheless, could not be monitored during the course of this study.

Table 5
Percent methane content in biogas from the experimental reactors.

Sampling for GC analysis	FE1	FE2	FE + SS1	FE + SS2	FE + AFG1	FE + AFG2	FE + LME1	FE + LME2	FE + DME1	FE + DME2
Sampling 1 (wk 1)	50	55	49	48	45	51	50	46	47	47
Sampling 2 (wk 2)	52	54	49	49	49	47	46	45	52	48
Sampling 3 (wk 3)	57	57	52	58	63	60	50	51	55	55
Sampling 4 (wk 4)	65	63	61	59	61	62	59	60	58	57
Sampling 5 (wk 5)	72	70	65	68	67	67	66	69	62	65
Sampling 6 (wk 5)	73	72	67	69	72	70	75	72	68	73
Sampling 7 (wk 6)	69	72	65	65	68	71	72	72	71	70
Sampling 8 (wk 7)	68	67	66	67	68	68	70	69	71	69
Sampling 9 (wk 9)	65	62	61	60	60	62	67	66	63	67

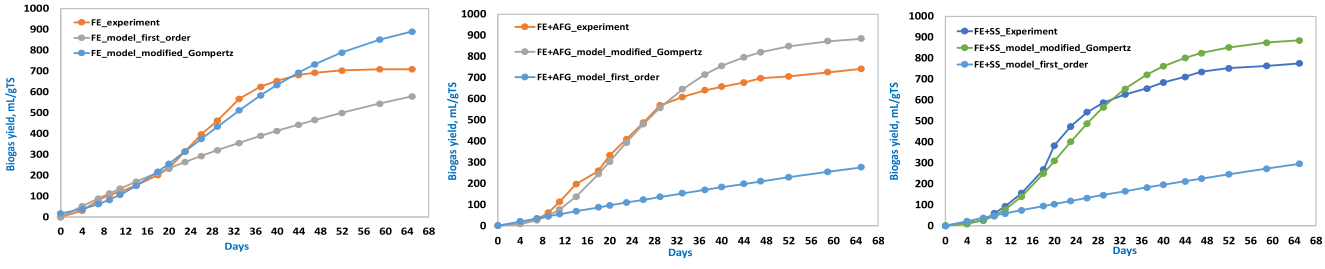

Fig. 4. Comparison between measured and predicted biogas yield using first order and modified Gompertz model.

4. Conclusions

The present work assessed the biogas potential of fish ensilage and four fish-oil refinery by-products: soapstock, alkaline fish glycerine, light mono-esters and dark-mono esters through batch mode co-digestion experiment. As the results revealed, more accumulated biogas can be obtained from the co-digesters compared to the FE digesters alone. The maximum average 2 times increase was obtained from the FE + LME reactors corresponding to extra ~1100 kWh/ton of energy yield worth ~0.892 ton of CO_2 savings. Likewise, mono-ester co-digesters FE + DMEs produced 1.8 times more biogas than the mono-digesters FEs. SS and AFG co-digesters produced almost similar amount of biogas with approximately 1800 mL at the end of the experiment. In terms of specific biogas yield (mL/gTS), soapstock co-digesters gave the highest yield with the amount 775 mL/gTS, followed by FE + AFG and FE respectively. As for e methane content, the periodic increase as with experiment progress was evidenced. While the maximum measured methane content of about 75% was resulted in one occasion from the reactor FE + LM1 at week 5, the average value from all the reactors kept over 61% throughout the course of the experiment.

In terms of kinetic analysis of the data, modified Gompertz model seemed to have better fitted with the measured biogas yield for all the reactors compared to those from the first order kinetics model. Since the current study did not include the experimental data on the influence of VFA, ammonia and other parameters on biogas yield, the provided kinetic analysis is an only indication to the anaerobic digestion efficiency. Thus, an extended research involving the effect of the above parameters on AD performance should be considered in future perspective.

Author Statement

Shiplu Sarker: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing original draft, Writing review and editing, Visualization, Supervision, Project administration. Microsoft Excel: Software. NTNU and Biokraft: Resources. ENERSENSE, NTNU: Funding acquisition

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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