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Biogasification Potential

Biogasification Potential of Desugarized Molasses from Sugarbeet Processing Plants

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ABSTRACT

Sugar production from sugarbeet (Beta vulgaris) generates a co-product stream called raffinate, desugarized molasses, or concentrated separated by-product (CSB). About 0.25 metric tonnes of raffinate is generated for every metric tonne of sugar produced. In this paper, the potential of biogasifying the raffinate to produce methane fuel is investigated. Several aliquots of CSB raffinate (0.1 - 0.2 kg), obtained from the American Crystal Sugar Company, MN, were biogasified in batch mode in a bench-scale anaerobic downflow stationary fixed film reactor (DSFFR) at a thermophilic temperature of 55 °C. It was found that about 0.118 m³ of methane at STP was produced per kg raffinate. This volume of methane was recovered in the biogas within a 2 day period indicating very good degradability. For every kg of raffinate fed into the anaerobic digester about 94 g COD of organic matter will be discharged with the digester effluent along with 27 g of microbial biomass (or sludge). Every metric tonne of raffinate can generate 4,300 MJ (3.7 MMBtu/US ton) of thermal energy from the combustion of the methane or about 300 kWh, of electricity can be generated (assuming 25% efficiency of converting thermal energy to electricity).

Additional key words: Anaerobic digestion; biogas; raffinate; CSB; sugar beet

Nearly 40% of refined sugar consumed in the USA is produced from sugarbeet (Beta vulgaris L.). Beet sugar processing generates significant quantities of both solid (tailings, spent pulp) and liquid (molasses, wastewater) by-products and organic wastes. For example, American Crystal Sugar Company, East Grand Forks (EGF) plant processes 8,310 (metric) tonnes of sugar beets daily to produce 1320 tonnes of sugar. The plant also produces 3500 m³ of wastewater, 432 tonnes of tailings, 1273 tonnes of pressed spent pulp and 332 tonnes of desugarized molasses (Polematidis et al., 2008). The molasses stream from the crystallization process is usually further desugarized in chromatographic separators to recover about 70% of the sucrose. The desugarized molasses by-product stream contains water, residual sugars, raffinose, betaine, amino acids, nitrogen compounds, organic acids and inorganic salts. In some plants the betaine is recovered as another value added product. The desugarized molasses stream is concentrated (also called concentrated separated by-product, CSB raffinate) and sold as animal feed for about US\$20/tonne.

Sugar production from sugarbeet is an energy intensive operation due to the need for drying and evaporation, and a variety of fossil fuels including coal and natural gas are used. In this paper, we investigate the potential of converting CSB raffinate stream into biogas fuel. Biogas produced in this manner would be a renewable biofuel and could potentially displace some of the fossil fuel used in the plant. Biogasification (or anaerobic digestion) is a biochemical process in which the organic compounds (like carbohydrates, proteins and fats) are mineralized to biogas under anaerobic conditions by the concerted and syntrophic action of a mixed culture of naturally occurring microorganisms. Biogas is a mixture of methane (50 - 70%) and carbon dioxide (30-50%) and can be used as fuel in boilers or for electricity generation with very little clean up. Biogas can also be converted to renewable natural gas by removing carbon dioxide and other trace contaminants and injected into natural gas pipelines for transportation. The process of anaerobic digestion has advantages over aerobic waste treatment processes since it not only reduces the polluting potential (oxygen demand) of the waste but also produces a biofuel. The process does not reduce the nutrient (nitrogen and phosphorus) levels.

Even though there have been some studies pertaining to anaerobic digestion of molasses from sugarcane refineries (Romli et al., 1994, 1995), it is not implemented in practice as molasses in itself has a high value and by converting to biogas not much value is added to the feedstock. However, the situation may be different for the desugarized molasses stream as it is a low value product. Moreover, since a major

fraction of the sugars have been removed, its methane production potential could have also decreased and may not produce significant methane to make its biogasification economically viable. This paper presents results from laboratory scale investigations on the biochemical methane potential of desugarized molasses from a sugarbeet processing plant. The anaerobic digestion process is analyzed in terms of extent of organic matter converted to biogas, undegraded residual organic matter and methane production rate. Based on the results a simple analysis was carried out to determine energy potential of the raffinate.

METHODS

Anaerobic Digester.

Experiments were conducted in a 20 liter anaerobic filter digester made from a Pyrex glass (Figure 1). The carboy was thermally cut at its base and a flanged lip was curled, resulting in an inverted bottle with a complete cross-sectional opening at the top. The neck of the bottle was adjusted by thermally fusing a glass flange to increase overall length. A 316 stainless steel lid was mounted on the curled flanged lip and held by twelve wing-nut bolts and a silicon gasket. This provided sufficient sealing for near ambient pressures that would be experienced in the digester. A custom-build glass Duran O-ring flange bottom was machined to fit the carboy-neck flange, and was secured by a stainless steel, quickrelease clamp. The vessel was filled with packing media (landscaping lava rocks) occupying a volume of 16 L (69% porosity) and were supported over a screen. The liquid volume below the bed was 2 liters and the headspace was maintained at a constant volume of 2 liters. The working volume of the digester was 18 L, with a liquid volume of 11 L. Ports (1/4-3/8 inch) on the top of the lid and glass-flange at the bottom of digester were used for leachate recirculation (via a peristaltic pump, $\sim 0.42 L/min$), gas outlet and sample collection. The vessel and its contents were heated by two flexible electric heating tapes (Thermolyne BriskHeat©, Waltham, Massachussetts) and was insulated by fiber glass insulation. The temperature was monitored by a T-type thermocouple (Omega, Stamford, Connecticut) probe. An on-line pH probe (Campbell Scientific© CSIM 11, Logan, Utah) was mounted in an external flow cell within the leachate re-circulation line; pH of leachate was monitored continuously. The temperature, pH and gas production were logged by a data logger/control module (CR10X, Campbell Scientific, Inc, Logan, Utah) and later retrieved into a PC. The control module also controlled the temperature of the digester contents at a pre-determined set-point by turning on/off the heating tapes. Gas production from the digesters was measured using a positive displacement gas meter. Details of construction of gas meter are given in Koppar and Pullammanappallil (2008).

Feedstock.

CSB raffinate was provided by American Crystal Sugar Company (ACSC), from its East Grand Forks, Minnesota plant in a 5 gallon bucket and was stored at room temperature. The typical characteristics (not necessarily for the sample shipped to our laboratory) of CSB raffinate from East Grand Forks factory as measured by American Crystal Sugar Company (ACSC) are listed in Table 1. In addition, the following organic matter compositions were also reported: protein - 12.3%, fat - 0.216%, volatile fatty acids - 1.42%, nonvolatile fatty acids (mainly lactic acid)



Fig. 1. Schematic diagram showing set up of the digester.

- 11% and total sugars (as invert) - 19%. These compositions were used to estimate a theoretical chemical oxygen demand for raffinate which was then compared to the COD value measured in the laboratory.

Anaerobic digestion protocol.

Aliquots of 0.1 kg – 0.2 kg (weight as received) of CSB were injected into the digester for each phase of the experiment. The digester was operated at thermophilic temperature (55 °C) and was inoculated with 13 L (0.013 m³) of mixed liquor taken from a thermophilic digester that had been digesting sugarbeet tailings for over a year. The mixed liquor contained active populations of microbial communities required for anaerobically digesting organic matter. The order, families or species within these communities were not identified. Once the gas production from the first experimental phase declined, more CSB raffinate was injected and digestion allowed to proceed. This was repeated four more times.

Analysis.

Samples of biogas from the digester were analyzed for methane and carbon dioxide using a GC equipped with thermal conductivity detector, and hydrogen sulfide using a Draeger tube (Sugarland, Texas). The liquid samples were analyzed for soluble chemical oxygen demand (sCOD) and sulfate-S using a Hach kit (Loveland, Colorado) and volatile organic acids using a GC equipped with flame ionization detector. Dry matter and volatile matter content of the raffinate was also measured. Details of these analytical procedures have been explained in Polematidis et al., (2008). Cumulative methane production for each experiment from the digesters was evaluated by fitting this data to the modified Gompertz equation (Polematidis et al., 2008).

RESULTS

Characteristics of desugarized molasses.

A comparison of moisture content, volatile solids and ash content measured in our laboratory with that reported by ACSC show that these are in good agreement (Table 1). The chemical oxygen demand (COD) value provides information on the organic content of a sample and it is the amount of oxygen required to chemically oxidize the organic matter. Theoretical values of COD can be calculated for known chemical compounds or from molecular (or empirical) formula. The organic matter in raffinate (sugars, protein, fat and volatile and non-volatile organic acids) when converted to a theoretical chemical oxygen demand (COD) yields approximately 0.49 kg COD/kg. The total theoretical oxygen demand was calculated by summing up the theoretical chemical oxygen demand of individual components using model molecules to represent these compounds. Theoretical chemical oxygen demands of individual components were 1.067, 1.067, 1.067, 2.89, 1.37 gCOD/g for sugars (represented as glucose), lactic acid, volatile fatty acid (acetic acid), fat (oleate-triglyceride) and protein (collagen or casein) respectively. This value was also in fair agreement with the COD value of 0.54 measured in our laboratory. Sulfate-S was measured to be 95 mg/L in a 50 g/L raffinate solution using a Hach kit. This was equivalent to 1900 ppm of sulfate-S or 5700 ppm of sulfate. This is in agreement with the sulfate concentration of 4880 ppm measured by ACSC (Table 1).

Biogasification of desugarized molasses.

Profiles of volumetric methane production rate (i.e. volume of methane produced per active volume of digester per day) and cumulative methane yield from all five phases of the experiment are shown in Figure 2 and Figure 3, respectively. In the first three phases (Phases I – III) aliquots of 0.1 kg (as received) were used, in Phase IV 0.15 kg was used and in Phase V 0.20 kg was used. All five phases of the experiment were conducted over a period of 14 days. Phase I was initiated by adding inoculum. The digester was not reinoculated for the next four phases.

(ACSC).			
Parameter	Units	Value	ACSC
		(this study)	values
Moisture	%	25	29.6
Dry matter (dm)	%	75	70.4
Volatile Solids (VS)	% dm	78	
	%	58.5	51.3
Ash	% dm	22	
	%	16.5	19.1
Density	g/ml	1.33	
COD	kg COD/m ³	719	
COD to Mass	kg COD/kg raffinate	0.54	
Sulfate (SO_4-S)	Ppm	1900	4880^{\dagger}

 Table 1. Characteristics of desugarized molasses measured in this

 study compared to those reported by American Crystal Sugar Company

 (ACSC)

[†] Reported as sulfate.



Fig. 2. Profile of methane production rate for batch digestion.



Fig. 3. Profile for cumulative methane yield for batch digestion.

In Phase I, the methane production rate peaked at 1.63 m³m⁻³ d⁻¹ in just 0.14 days, indicating rapid methanogenesis. After 1.6 days the methane rate dropped to 0.18 m³m⁻³ d⁻¹ and dropped further to 0.1 m³m⁻³ d⁻¹ in ~2 days. The cumulative experimental methane yield was 0.246 m³ CH₄ at STP kg COD⁻¹ in 2 days by the end of Phase 1. In Phase II methane production rate peaked at 1.06 m³m⁻³ d⁻¹ within 0.16 days of introducing the feed and in Phase III to 1.44 m³m⁻³ d⁻¹ within 0.2 days. After 1.6 days the methane rate dropped to 0.22 m³m⁻³ d⁻¹ and 0.12 m³m⁻³ d⁻¹ in Phase II and Phase III, respectively. Methane rate dropped slower in Phase II than Phase III. Phase II and Phase III reached completion in ~3.2 and 1.8 days, when the daily methane production rate dropped to 0.029 and 0.043 m³m⁻³d⁻¹ respectively. The cumulative experimental methane yield was 0.223 m³ CH₄ at STP kg COD⁻¹ and 0.233 m³ CH₄ at STP kg COD⁻¹ at the end of Phase II and Phase III, respectively.

In Phase IV the amount of raffinate added was increased to 0.15 kg. Methane production rate peaked at 1.22 m³m⁻³d⁻¹ in 0.35 days. Phase IV reached completion in ~3.2 days when the daily methane production rate dropped to 0.048 m³m⁻³d⁻¹. The cumulative experimental methane yield was 0.190 m³ CH₄ at STP kg COD⁻¹ at the end of the phase. In Phase V the amount of raffinate added was further increased to 0.2 kg. The methane production rate peaked at 1.85 m³m⁻³d⁻¹ in just 0.29 days. The cumulative experimental methane yield was 0.190 m³ CH₄ at STP kg COD⁻¹ within ~2.5 days.

Residual organic matter after anaerobic digestion.

Figures 4 and 5 show the soluble COD, which combines all the chemically oxidizable organic matter (sCOD), and volatile organic acid concentrations in the digester during the entire experimental period which



Fig. 4. Profile of soluble COD concentration in the digester.

includes Phases I – V. Samples were analyzed at the beginning of the experiment and at the end of each phase. For Phases I and II intermediate samples during the phase were also analyzed. At the beginning of the experiment, the sCOD concentration was 2,280 mg L⁻¹ which was primarily non-degradable organics in the inoculum. Upon adding raffinate, this value increased rapidly to 5,000 mg L⁻¹ and with sustained methanogenesis decreased to around 2,000 mg L⁻¹ by the end of Phase I. The sCOD concentration at the end of subsequent phases fluctuated between 3,000



Fig. 5. Profile of volatile organic acids (VOAs) in the digester.

and 4,000 mg L⁻¹. The initial acetic acid, butyric and propionic acid concentrations in the batch digester were below the detectable limit of 50 mg L⁻¹. Upon addition of raffinate, the concentrations increased, especially those of acetic and propionic acid. These concentrations increased to 900 and 1150 mg L⁻¹ respectively and subsequently decreased. After every addition of raffinate, the concentration of acetic acid increased and then dropped. Concentration of acetic acid was highest at 1,100 mg L⁻¹ in Phase II. Propionic acid concentration also showed a similar trend, but the peak in Phase II occurred at 600 mg L⁻¹. By the end of the experiment, the concentration was around 200 mg L⁻¹. Concentrations of other higher chain organic acids like butyric and valeric stayed at 100 mg L⁻¹ or below in all samples.

DISCUSSION

The degradable organic matter as indicated by the sugar, protein and fat content of about 42% by weight in CSB raffinate is quite high. This indicated a good potential for biogasification. Upon introducing raffinate into the digester, it was rapidly degraded as seen from a quick increase in methane production rate which usually peaked within 8 hours (0.3 days). Subsequent drops in methane production were due to depletion of substrate. The cumulative methane data from the five phases was further analyzed quantitatively by fitting a modified Gompertz model. The model parameters for the ultimate methane yield that best fit the data are listed in Table 2. The model fit to the experimental data is shown in Figure 3. In all cases, the model satisfactorily followed the experimental trend. The average methane yield measured at standard conditions for temperature (273 K) and pressure (1 atm) was 0.218 m³ (kg COD of raffinate)⁻¹ which was equivalent to 0.118 m³ (kg raffinate)⁻¹ or 3,744.64 cubic foot (ton of raffinate)⁻¹. This volume of methane was produced within 2 days in a digester.

The ultimate cumulative methane yield (value predicted by model) obtained from the first three phases when 0.1 kg of raffinate was introduced varied between a narrow range of 0.231 and 0.254 m³ kg COD⁻¹. The average methane yield for these phases was 0.236 \pm 0.016 m³ kgCOD⁻¹. However, for phases 1V and V when the amount of raffinate was increased, the yield dropped to 0.190 \pm 0.007 m³ kgCOD⁻¹. It was concluded that a decrease in methane yield when a higher amount was loaded was not due to inhibition from compounds in raffinate, because the rates of methane generation were as rapid as it was when 0.1 kg was fed. It took around 2 days to produce 95% of ultimate methane in all cases. Any inhibition from compounds in the raffinate

would have caused methane rate to gradually drop from Phases I to V as toxins would have accumulated in the digester. This was not the case. The drop in methane yield could be due to the variability between aliquots of raffinate fed into the digester caused by settling upon storage. On average it can be expected that raffinate would produce about 0.218 m³ kg COD⁻¹ (or 0.118 m³ kg⁻¹) of methane and 95% of this quantity would be generated within 2 days. So an anaerobic digester designed to produce biogas from raffinate would be sized for a hydraulic retention time of at most 2 days.

The process of anaerobic digestion does not completely mineralize all organic matter in the feedstock, thus producing an effluent that will contain residual organics. The concentration of residual organics depends on the chemical nature of the organic compounds in the feedstock. Some of these are not amenable to biological degradation by anaerobes and remain in the treated effluent. Another source of residual organics is the intermediate volatile organic acids produced during anaerobic digestion. The anaerobic digestion process proceeds serially via first fermentation to a mixture of volatile organic acids (primarily acetic, propionic and butyric acids), conversion of the higher chain organic acids to acetic acid and methanogenesis from acetic acid. Methane is also produced from hydrogen and carbon dioxide that is evolved during the fermentation processes. Among the higher chain volatile organic acids, the concentrations of butyric and valeric acids remained low, < 100 mgL⁻¹, throughout the experiments. Propionic acid concentrations fluctuated at higher values at first, increasing upon introducing the feed and decreasing as it was consumed. However, towards

Experimental Phases	Experimental cumulative methane yield m ³ (kg COD) ⁻¹	Ultimate meth- ane yield from Gompertz model m ³ (kg COD) ⁻¹	Duration to produce 95% of ultimate yield days
I	0.246	0.254	2
II	0.223	0.224	2.5
III	0.233	0.231	1.5
IV	0.190	0.195	1.74
V	0.190	0.185	2.08
Average	0.216 ± 0.0254	0.218 ± 0.0279	1.96 ± 0.377

All gas volumes are reported at STP (273 K, 1 atm)

the later period of the experiment (Phases IV and V), the level of accumulation of propionic acid decreased, indicating that the digester had developed active populations of microorganisms that could consume propionic acid. Usually in an anaerobic digester consumption of higher chain volatile organic acids occurs at a slower rate and it is critical that these do not accumulate. Acetic acid was the primary volatile organic acid intermediate produced in the process. Immediately after feeding the digester it would increase to concentrations between 600 and 1000 mg L⁻¹ and then decrease quickly to around 200 mg L⁻¹ prior to the next feed. If each phase was carried out for a longer duration acetic acid levels could be brought to much lower values. Typically acetic acid concentrations in effluents from industrial anaerobic digesters vary between 50 and 500 mg L⁻¹ (Malina, 1992).

To verify the consistency of the data that was measured, a COD (chemical oxygen demand) balance was performed for each experiment. In an anaerobic digestion process, the COD introduced into the digester via the feed should equal the sum of COD of products (methane and new cell biomass), intermediate metabolites and undegraded feed. Even though carbon dioxide is a product, its COD is zero, so it does not appear in the COD balance equation. For each phase of the experiment, the COD balance equation for the digester would be

(Total COD of organic matter) in digester at start	=	COD of methane produced during the experiment + (Total COD of organic matter) in the digester at end
(Total COD of organic matter) $_{\rm in digester at start}$	=	\sum_{start} (Residual soluble COD + COD of feed)
(Total COD of organic matter) in the digester at end	=	$ \left\{ \begin{matrix} {\rm COD} \ of \ biomass + {\rm COD} \ of \ undegraded \ feed + \\ {\rm COD} \ of \ residual \ volatile \ organic \ acids + \\ {\rm COD} \ of \ discarded \ mixed \ liquor \end{matrix} \right\} \\ \end{matrix} \right\} $

Soluble COD concentration measurement at the end of an experiment is a lumped measure of the undegraded organic matter present in the digester mixed liquor and residual volatile organic acids. The methane produced during the experiment can be converted to COD units by using a conversion factor of 2.86 g COD (L of methane at STP)⁻¹. All terms in the above equation were measured during each experiment except for COD of new biomass. It was assumed that 10% of feed COD is directed towards production of new biomass (Chen et al., 2008). The COD balance for each experiment is shown as a stacked bar graph in Figure 6 comparing COD at the start with COD at the end for each experiment. Ideally, for a perfect COD balance, the height of the bars at the start of





the experiment should equal the height of the bars at the end of each experiment. It can be noted that this was not the case; however, the height of the bars are approximately equal within the errors associated with measurements. Some conclusions were drawn from the COD balance for individual experiments: 63-90% of COD in feed was converted to methane and 0-35% of COD in feed remained as residual COD. An overall COD balance was performed over the five experiments. In this approach, the sum of the COD at the start of the experiment and the total COD of feed added to the system during the five phases was equated to the sum of the CODs produced from the system as methane for the five phases, the CODs discarded in Phases III, IV and V, the CODs of biomass produced in the five phases and residual COD at the end of Phase V. The two sums were almost equal, the difference being merely 150 mg L⁻¹. From this balance, it was concluded that 76% of the feed COD was converted to methane which meant that every kg of raffinate would produce 0.143 m³ of methane at STP. About 17% of feed COD remained undegraded or as residual volatile organic acid intermediates. This means that the treated effluent from the digester will contain 94 g of COD for every kg raffinate fed. The effluent will also produce 27 g of biomass for every kg of raffinate. The effluent will contain nitrogen and phosphorous and can be land applied to recycle these nutrients. However, a digestion facility will need to incorporate systems to manage the biomass sludge and possible post treatment of residual volatile organic acids in effluent prior to land application.

Using the experimental methane yield of 0.118 m³ STP kg⁻¹ (or 3,744.638 scf/US ton), the energy content from a metric tonne of raffinate will be 4,300 MJ or 3.7 MMBtu/US ton. This calculation assumed that the biogas has been dried and carbon dioxide and other contaminants have been removed; therefore, the energy content would be that of the methane which has a heating value of 37 MJ/m³ STP or 1000 Btu per scf. The methane made by anaerobic digestion of all the raffinate produced daily, for example at the East Grand Forks factory (332 tonnes or 365 tons), can displace about 15% of the natural gas or coal used in the boiler houses in the factory (Polematidis et al., 2008). At 25% efficiency of converting thermal to electrical energy, this amount of methane may also be used to generate 4.2 MW of electricity. With a combined heat and power generation system, the waste heat could be used in boilers for steam generation in the plant. The biogas produced contained hydrogen sulfide resulting from the reduction of sulfate in the raffinate. Hydrogen sulfide content in biogas varied between 500 and 1200 ppm.

CONCLUSIONS

The following conclusions were made from the study:

• CSB raffinate was readily converted to biogas in an anaerobic digester. About 0.118 m³ of methane at STP was produced from 1 kg of raffinate. This volume of methane was recovered in the biogas within a 2 day period indicating very good degradability of raffinate.

• About 94 g COD of organic matter will be discharged with the digester effluent for every kg of raffinate that is fed to the digester.

• The effluent will also contain microbial biomass (or sludge) which is about 27 g for every kg of raffinate that is fed to the digester.

• Every metric tonne of raffinate can generate 4300 MJ (= 3.7 MMBtu/USton) of thermal energy from combustion of the methane produced by biogasification.

• About 300 kWh of electricity can be generated from methane made from 1 tonne of raffinate (assuming 25% efficiency of converting thermal energy to electricity).

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