## UDC: 60:664.2.033:663.93 METHANE FERMENTATION OF POMACE WASTES GENERATED IN CEREAL COFFEE PRODUCTION

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Batch methane fermentation of pomace wastes from cereal coffee production was experimentally studied. Data were elaborated with modified Gompertz kinetic model. The 10-time increase in reactor load 5-50 g/dm<sup>3</sup> corresponds to proportional growth of maximal biogas yield  $H_{max}$  from 421.94 to 4119.37 cm<sup>3</sup> and growth of maximum process rate  $R_{max}$  from 1.0745 to 10.7379 cm<sup>3</sup>/h. Unit reactor yield (for 1 g of raw mass, dry mass and dry organic mass) decreases, however, with increase in reactor load within 5-30 g/dm<sup>3</sup> range while unit maximum process rate turned out to be practically load-independent.

# Cereal coffee, pomace wastes utilization, biogas, batch methane fermentation kinetics, modified Gompertz model

According to Food and Agriculture Organization of the United Nations (FAO) 1/3 of the world's food produced is lost in a food chain. In many countries this food is landfilled or incinerated with organic fraction of municipal wastes for energy recovery. These biowastes can be also subject of fermentation resulting in production of convenient energy carriers as: biogas, hydrogen, ethanol or biodiesel [1].

Biogas can be also manufactured in co-fermentation of natural coffee wastes with animal metabolic products. In mesophilic conditions during 8 months of fermentation about 60% of organic substance can be transformed [2]. Natural coffee wastes can be also used for biogas production independently [3,4]. During fermentation of natural coffee wastes many interesting compounds is produced like alcohols, esters, aldehydes, terpenes

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as well as volatile organic acids [5], proteins and fats [1], polyphenols, tannins and caffeine [6].

Cereal coffee is one of the most often used food industry products. It is manufactured based on various cereals, complemented with other plants like chicory and sugar beets according to specific needs for appropriate taste results [7]. It can be regarded as a substitute of natural coffee characterized by high caffeine level. During its production bioorganic wastes are generated which should be utilized according to sustainable development rules, considering also economical aspects and constraints. Considering production level in a large (World or country) scale, proper utilization of these wastes is a serious problem. Optimal utilization should consider its direct conversion into cogeneration of heat and electricity) or energy (e.g. biochemical transformation route into energy carriers convenient (biomethane. biohydrogen).

Possible thorough characteristic of solid wastes from cereal coffee production is crucial for methane fermentation of these substances. Carbohydrates, proteins, fats and plant fibres content is important for determination of the biogas yield and process kinetics. Modern spectroscopy techniques seem to be useful for cereal coffee biowastes biodegradability determination [8].

In the accessible literature some examples of practical developing of residuals from cereal coffee production are reported. However, use of these biowastes mainly as a co-substrate in various energetic applications (as biomass for co-incineration with coal) is reported [9-11]. In consequence of biomass thermal decomposition (pyrolysis, gasification) some corrosion problems arise, practically inhibiting further application of this energetic technology. An alternative, ecological approach can be methane fermentation process of these wastes, classified as organic recycling [9]. Technological wastes from cereal coffee production can be also used as a fraction of multicomponent biomass substrates. Nevertheless, final methane production effects are reported for the complex mixture as a whole, without more detailed information of the effect's subdivision into each component (its intrinsic contribution). This way one can notice in literature practically lack of reliable data concerning individual contribution of the cereal coffee postproduction wastes to methane production, crucial for objective evaluation of its applicability in this promising energetic application.

**Objective of the Paper.** Main purpose of the presented study was laboratory investigation of anaerobic fermentation potential of residuals and wastes from cereal coffee production line (mainly pomace wastes), as well as making experimental insight into anaerobic fermentation process kinetics (batch variant), which is the basis for biogas plant design and economic evaluation of its performance.

**Presentation of the Research.** Thermostated (38°C, external water bath) glass laboratory reactors especially designed for anaerobic fermentation processes research (Fig. 1), of working volumes 1 dm<sup>3</sup> were used. Inoculum and: 5, 10, 20, 30 and 50 g, appropriately, of mechanically disintegrated pomace wastes from cereal coffee production line (Fig. 2-3) were used as a basic reactor loads. Analytically determined composition of research object (5 samples for statistical verification) is presented in Table 1. In defined time lags global volume of the produced biogas was systematically registered followed by current analysis of its composition. Detailed presentation of experimental methodology and plant construction is presented elsewhere [12].



Fig. 1. Experimental plant for methane fermentation tests of cereal coffee wastes



Fig. 2. Photo of cereal coffee wastes before anaerobic digestion (raw substrate)

The experimental results representing batch anaerobic fermentation process effects were registered as cumulative gaseous product volumes, then diminished by intrinsic inoculum contribution to biogas production (comparative parallel tests) and finally subject of kinetic analysis based on modified Gompertz model (1) [13]:

$$H = H_{\max} \exp\left\{-\exp\left[\frac{R_{\max}e}{H_{\max}}(\lambda - t) + 1\right]\right\}$$
(1)

reflecting specific sigmoid course of batch fermentation process, with possibility of direct calculation of kinetic process parameters  $H_{max}$ ,  $R_{max}$  and  $\lambda$ , where:

,

*H* – cumulative biogas volume produced up to time *t*, cm<sup>3</sup>; H<sub>max</sub> – maximal (asymptotic) H, cm<sup>3</sup>; R<sub>max</sub> – maximum process rate, cm<sup>3</sup>//h;  $\lambda$  – lag phase (incubation) time, h; t – process time, h.

#### 1. Cereal coffee postproduction wastes (pomace wastes) – analytical determination of samples composition before anaerobic fermentation tests

Dry mass	Organic mass	Inorganic	Moisture	Organic				
fraction	fraction [%]	mass fraction	fraction	fraction in				
[%]		[%]	[%]	wet mass [%]				
22.814	97.031	2.969	77.186	22.137				
21.247	97.092	2.908	78.753	20.729				
22.280	97.135	2.865	77.72	21.641				
21.975	97.143	2.857	78.025	21.347				
23.283	97.218	2.782	76.717	22.635				
22.320	97.124	2.876	77.680	21.698				
	Dry mass fraction [%] 22.814 21.247 22.280 21.975 23.283 22.320	Dry mass fraction [%]Organic mass fraction [%]22.81497.03121.24797.09222.28097.13521.97597.14323.28397.21822.32097.124	Dry mass fraction [%]Organic mass fraction [%]Inorganic mass fraction [%]22.81497.0312.96921.24797.0922.90822.28097.1352.86521.97597.1432.85723.28397.2182.78222.32097.1242.876	Dry mass fraction [%]Organic mass fraction [%]Inorganic mass fraction [%]Moisture fraction [%]22.81497.0312.96977.18621.24797.0922.90878.75322.28097.1352.86577.7221.97597.1432.85778.02523.28397.2182.78276.71722.32097.1242.87677.680				



Fig. 3. Microscope images of cereal coffee wastes before anaerobic digestion (raw substrate) (optical microscope *OLYMPUS CH30*, magnification 10×)

Recalculated with kinetic model (1) experimental data (nonlinear regression) are presented in Table 2 in a form of:  $H_{max}$ ,  $R_{max}$  and  $\lambda$  for various reactor loads (5–50 g/dm<sup>3</sup> of reactor working volume). In Table 3 the data recalculated for 1g of raw mass (unit reactor load), 1g of dry mass and 1g or dry organic mass, appropriately, are presented for comparison. From the data analysis one can conclude that with the increase in reactor load from 5 to 50 g/dm<sup>3</sup> increase in maximal cumulative biogas volume produced (asymptotic sigmoid model (1) prediction) increases from 421.94 up to

4119.37 cm<sup>3</sup>. In the same time maximum process rate increases from 1.0745 up to  $10.7379 \text{ cm}^3/h$ .

experimental data elaborated with modified Gompertz model								
Reactor load [g/dm <sup>3</sup> ]	$R^2$	$H_{\rm max}$ [cm <sup>3</sup> ]	R <sub>max</sub> [cm <sup>3</sup> /h]	λ [h]				
5	0.998	421.94	1.0745	35.08				
10	0.998	826.13	2.1512	46.93				
20	0.998	1648.82	4.2962	47.06				
30	0.998	2414.19	6.4118	46.01				
50	0.998	4119.37	10.7379	47.06				

2. Maximal cumulative biogas volume produced, maximum process rate and lag phase (incubation) time for reactor loads 5–50 g/dm<sup>3</sup> –

Both quantities are roughly load-dependent since 10-time increase in reactor load results in nearly 10-time growth both in  $H_{max}$  and  $R_{max}$ . Increase in lag phase (incubation) time  $\lambda$  from ca. 35 h (Table 2, No. 1) up to 46–47 h (No. 2–5) can be observed, however it may be partly attributed to experimental error effect. Analysing data from Table 3, representing unit yield and unit conversion rate, some additional information can be gathered. With the increase in reactor load from 5 to 30 g/dm<sup>3</sup> unit maximal vield, based on 1g of raw mass, decreases (84.39  $\rightarrow$  80.47 cm<sup>3</sup>/g). One can thus conclude, that higher reactor load with pomace wastes from cereal coffee production line corresponds to systematically decreasing conversion yield. Similar conclusions can be drawn in respect to unit yields representing 1g of dry mass (378.08  $\rightarrow$  360.54 cm<sup>3</sup>/g) and 1g of dry organic mass (389.28  $\rightarrow$  371.22 cm<sup>3</sup>/g), respectively. Analyzing the  $R_{\rm max}$ data in Table 3 one can conclude, that maximal unit process rates vary only insignificantly in all three cases, thus it can be assumed that these are load-independent. Considering data from Table 3 one can also conclude, that from 1 Mg of raw cereal coffee postproduction wastes (pomace biowastes) it is possible to obtain from 84.39 to 80.47m<sup>3</sup> (mean 82.46m<sup>3</sup>) of biogas depending on reactor load applied  $(5 - 30 \text{ kg/m}^3)$ . From 1Mg of dry mass and 1Mg of dry organic mass these yields vary from 378.08 to 360.54 m<sup>3</sup> (mean 369.45 m<sup>3</sup>) and from 389.28 to 371.22 m<sup>3</sup> (mean 380.39 m<sup>3</sup>). appropriately.

# 3. Maximal unit cumulative biogas volume produced and maximal unit process rate – data from Table 2 recalculated for: 1g of raw mass, 1g of dry mass and 1g of dry organic mass

Recalculated for:

	1g of raw mass			1g of dry mass			1g of dry organic mass		
No	$R^2$	H <sub>max</sub> [cm <sup>3</sup> /g]	R <sub>max</sub> [cm <sup>3</sup> /g/h]	$R^2$	H <sub>max</sub> [cm <sup>3</sup> /g]	R <sub>max</sub> [cm <sup>3</sup> /g/h]	$R^2$	H <sub>max</sub> [cm <sup>3</sup> /g]	R <sub>max</sub> [cm <sup>3</sup> /g/h]
1	0.998	84.39	0.2149	0.998	378.08	0.9628	0.998	389.28	0.9913
2	0.998	82.61	0.2151	0.998	370.13	0.9638	0.998	381.09	0.9924
3	0.998	82.44	0.2148	0.998	369.36	0.9624	0.998	380.30	0.9909
4	0.998	80.47	0.2137	0.998	360.54	0.9576	0.998	371.22	0.9859
5	0.998	82.39	0.2148	0.998	369.12	0.9622	0.998	380.05	0.9907
Mea	an:	82.46	0.2147		369.45	0.9618		380.39	0.9902

**Conclusions.** Batch anaerobic fermentation of pomace wastes from cereal coffee production was investigated. Based on modified Gompertz model process kinetics was elaborated. Increase in reactor load 5-50 g/dm<sup>3</sup> corresponds to maximal biogas yield from 421.94 to 4119.37 cm<sup>3</sup> and maximum process rate from 1.0745 to 10.7379 cm<sup>3</sup>/h. Unit reactor yield decreases with the increase in reactor load 5-30 g/dm<sup>3</sup> (84.39  $\rightarrow$  80.47, 378.08  $\rightarrow$  360.54, 389.28  $\rightarrow$  371.22 cm<sup>3</sup>/g, for 1g of raw mass, 1g of dry mass and 1g of dry organic mass, respectively). Maximal unit process rate turned out to be load-independent. The data can be used in a batch biogas plant design or economic evaluation of its loading strategy.

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У статті наведено результати експерименту метанового бродіння кавових відходів. Експериментальні дані були оброблені за допомогою кінетичної моделі Гомперца.

З'ясовано, що збільшення у 10-разів навантаження реактора 5-50 г/дм<sup>3</sup> призводить до пропорційного зростання виділення біогазу H<sub>max</sub> від 421,94 до 4119,37 см<sup>3</sup>. Також відбувається прискорення швидкості процесу виділення біогазу R<sub>max</sub> від 1,0745 до 10,7379 см<sup>3</sup>/год. Результати свідчать, що продуктивність одного реактора (на 1 г сирої, сухої і сухої органічної мас) зменшується, однак, встановлено, що зі збільшенням навантаження реактора в 5-30 г/дм<sup>3</sup>, діапазон швидкості процесу практично не змінюється, тобто не залежить від навантаження.

Зернова кава, утилізація відходів, біогаз, метанове бродіння, кінетика, модифікована Гомперц модель

В статье представлены результаты эксперимента метанового брожения кофейных отходов. Экспериментальные данные были обработаны с помощью кинетической модели Гомперца. Определено, что увеличение в 10 раз нагрузки реактора 5-50 г/дм3 приводит к пропорциональному росту выделения биогаза  $H_{max}$  от 421,94 до 4119,37 см<sup>3</sup>. Также, происходит ускорение процесса выделения биогаза  $R_{max}$  от 1,0745 до 10,7379 см<sup>3</sup>/ч.

Результаты свидетельствуют, что производительность одного реактора (на 1 г сырой, сухой и сухой органической масс) уменьшается, однако, установлено, что с увеличением нагрузки реактора в 5-30 г/дм<sup>3</sup>, диапазон скорости процесса практически не меняется, то есть не зависит от нагрузки.

Зерновой кофе, утилизация жмыховых отходов, биогаз, метановое брожение, кинетика, модифицированная Гомперцмодель.