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PRODUCTION OF BIOGAS FROM WASTE ANIMAL FATS

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Annotation. *The research results concerning biogas production from waste animal lard are presented. During preparation of various fried dishes with the use of lard or vegetable fats, modification of fats composition is observed. These undergo essential chemical transformations into more or less harmful products. Synthesized toxic substances dissolved in fats make, that these fats are no longer suitable for consumption or further use, thus should be safely finally utilized. Waste fats after the production of fried potatoes, doughnuts, fried meat, etc. are, however, regarded as attractive raw materials for biogas production. Laboratory analysis of anaerobic fermentation process of waste animal lard suggests, that its energetic utilization can be promising source of renewable energy. From 1 Mg of waste lard it is possible to produce in anaerobic fermentation ca. 620–720 m3 of good quality biogas, with maximum production rate varying from 1.067 to 1.082 dm3/kg d.m./h.*

Key words: ***wastelard, animal fat, biogas, biowaste utilization, batch anaerobic fermentation kinetics, modified Gompertz model***

General Outline of the Problem Discussed. During frying of lard or vegetable fat essential changes in its chemical composition are observed. Vegetable fats containing non-saturated fatty acids are subject of specific transformations. Decomposition of fats into fatty acids and glycerin was confirmed analytically. Heating in higher temperature favors production of toxic aldehydes and ketones. Dehydration of glycerin in high temperature conditions

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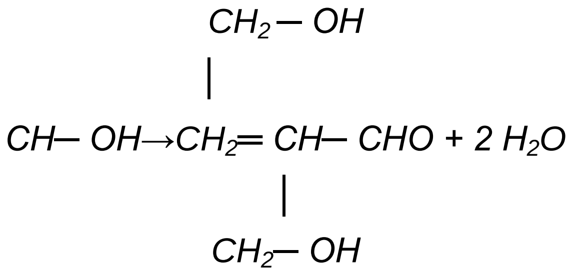
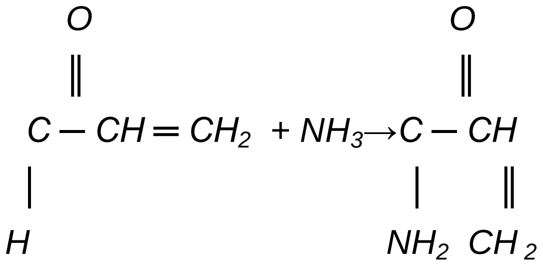
leads to formation of acrolein. Heating of fats with large fraction of protein and carbohydrates favors formation of acrylamide.

These chemical transformations can be presented with the following stoichiometric reaction schemes:



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH\rightarrow CH_2=CH-CHO+2\,H_2O \\ | \\ CH_2-OH \end{array}$$

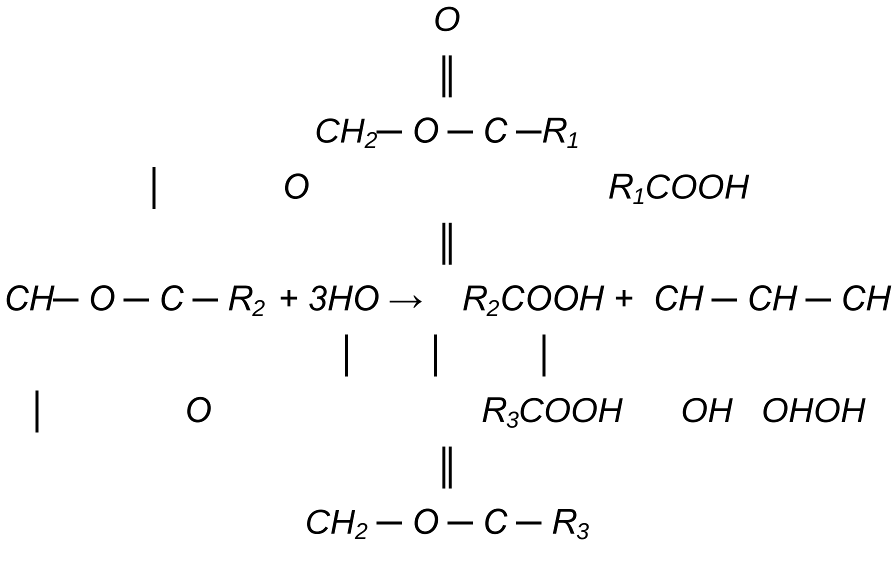
Acrolein in presence of ammonia can also transform into toxic acrylamide:



$$\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}-CH=CH_2+NH_3\rightarrow\underset{\underset{NH_2}{|}}{\overset{\overset{O}{\|}}{C}}-\underset{\underset{CH_2}{\|}}{CH}$$

AcroleinAcrylamide

The fats are subject of hydrolysis according to the following stoichiometric reaction scheme:



$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-R_1 \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-R_2+3HO\rightarrow\begin{array}{l}R_1COOH\\R_2COOH\\R_3COOH\end{array}+\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH}-\underset{\underset{OH}{|}}{CH} \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-R_3 \end{array}$$

Melting point of the lard, commonly used animal-derived solid fat, is between 38–42 °C. The frying process takes place in temperature above 100 °C, usually 150–200 °C. In the fats and oils the following toxic compounds are formed:

- oxidation products: peroxides and hydroperoxides, epoxides;
- cyclisation products: cyclic monomers.

During frying process also multiring aromatic hydrocarbons are formed, which demonstrate genetoxic, mutagenic and carcinogen properties. The higher temperature and time of the fat's thermal processing, the larger content of polycyclic aromatic hydrocarbons is detected.

Moreover, in animal fats being the subject of thermal processing one can confirm presence of:

- monomers and cyclic polymers;
- hydroxyacids;
- polycyclic aromatic hydrocarbons;
- oleinianacid;
- heterocyclic aromatic amines, trimethylamine;
- nitrosoamines;
- acetaldehyde;
- formaldehyde;
- naphtalene;
- mercaptanes.

During smoking the lard gains additional toxic compounds, including:

- alcohols: methanol;
- aldehydes: acetaldehyde, formaldehyde;
- ketones: acetone;
- phenols;
- carboxylic acids: formic acid, acetic acid.

Main source of waste animal fats in Poland are: calves, pigs, sheep, horses, rabbits, game meat, etc.

Analysis of Recent Studies and Publications. In the present day main technological trend in utilization of waste animal fats is biodiesel production. Biodiesel is usually produced as a substitution of conventional fuel based, however, on non-renewable resources. It is made of edible fats and vegetable oils. For biodiesel production the cheap and easily accessible raw materials are still required [1]. Waste animal fats (chicken fat, lard, tallow) derived from meat processing industry can be considered as one of the options. Methanol and ethanol are used in transesterification reactions involving waste animal fats [2]. Main possibilities of waste animal fats utilization as the cheap substrates in biodiesel production are presented in [3].

Main components of animal fats are, depending on their origin:

- chicken fat: oleic, palmitic, linoleic;
- duck tallow: oleic, palmitic, linoleic;
- mutton fat: oleic, palmitic, stearic;
- lard: oleic, palmitic, linoleic;
- yellow grease: oleic, palmitic, stearic;
- brown grease: oleic, palmitic, stearic, linoleic.

Interesting technological option can be application of waste vegetable biomass for the production of fats via *Hermetiaillunces* larva breeding on waste fruits and cakes produced from the grains. The natural larva fats are then subject of esterification in presence of sulfuric acid as catalyst. Produced this way methyl esters of fatty acids are used as the engine fuels [4].

In the world-scale significant amount of animal fats is produced, which can not be used any more, thus generating wastes. These can be potentially converted into biodiesel fuel. Most of these methods involve catalytic decomposition in basic environment. It turned out that very effective catalyst for transesterification reaction can be tetramethylammonium hydroxide. Conversion of fat into ester runs with the yield reaching even 98% [5].

In result of fats hydrolysis process their decomposition into the products soluble in water phase is observed. Efficiency of extraction from aqueous phase depends on polarity of these acids. The extracted fatty acids are then subject of esterification with methanol [6]. Also some method of biodiesel production based on swine manure substrate via housefly larvae (*Musca domestica* L.) [7] or from waste fish oil [8, 9] are presented in literature.

One of the options may be also thermal degradation (thermal cracking, fast pyrolysis) of fats like waste cooking oil. It was considered and experimentally tested in 475–525 °C [10]. Other study used moving bed pilot scale plant operated in 410–450 °C [11]. The cost effective, medium temperature conversion processes of, among other, animal fats are also considered [12].

Renewable substrates rich in fat can be also considered for sustainable biohydrogen production in dark fermentation process [13,14]. However, further implementation of these technologies in industrial scale is strictly connected with transformation of global energetics towards compatibility with hydrogen fuel, what is planned for nearest future.

Waste fat derived from wastewater treatment plant can be also used for biomethane production. Dehydrated waste fat from the fat catcher resulted in 606 cm^3 CH_4/g whereas sediment from municipal wastewater treatment plant was able to produce 223 cm^3 CH_4/g only [15]. Production technology of high quality fuel for jet engines from animal fats is known. The conversion process involves hydrooxygenation and hydrodecarboxylation, as well as consecutive hydroisomerisation reaction. The catalysts in a form of nickel and molybdenum oxides are used in this process. These are regarded to be very active in hydrotreating process, while platinum and palladium catalysts immobilized on zeolites are used as the hydroisomerisation catalysts [16].

During these processes also the following transformations run:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

$$CO_2 + H_2 \rightarrow CO + H_2O$$

It was concluded, that the best raw material for biofuel production is poultry fat. The poultry slaughterhouses are potential producers of large amount of lard. In Poland waste animal fats from slaughterhouses and after utilization are produced in amount of ca. 63 000 Mg/year. Biogas potential of various fats is discussed in respect to biorefinery [17], co-digestion [18,19], pre-treatment, optimal digester design [20], potential socio-econo-environmental impacts [21], as well as the possibilities of recovery and utilization of environmentally harmful effluents and wastewaters from various meat processing industries [22,23,24]. The authors own studies and observations (Fig. 1–4) suggest, that methane fermentation process can be optimal route for utilization of large amount of waste animal fats, producing ecological energy carrier in low temperature conditions and partially solving the odour problems resulting from these animal fats storage and their eventual spontaneous chemical decomposition reactions.

Fig. 1. Industrial broiler hens breeding (photo: Jan Cebula)

Fig. 2. Storehouse for hens excrements with waste fat (photo: Jan Cebula)


Fig. 3. Proportioner of fat-containing biomass into anaerobic fermentation chamber (photo: Jan Cebula)


Fig. 4. Preliminary storehouse for liquid fats used for feeding the anaerobic fermentation chamber (photo: Jan Cebula)

Objective of the Paper. The work focuses on identification in laboratory conditions the possibility of waste lard utilization in a process of methane fermentation. Process data are interpreted with modified 3-parameters Gompertz kinetic model, providing valuable information concerning maximal process yield, maximal process rate, as well as bacteria adaptation period (lag phase duration). The data presented can be used in design, redesign or/and economic evaluation of the existing biogas bioreactor performance.

Presentation of the Research. Substrate preparation. For the methane fermentation tests the obsolete lard derived from the commercial store was used. The research was done in Silesian University of Technology in Gliwice (scientific laboratory in Faculty of Energy and Environmental Engineering, Institute of Water and Wastewater Engineering, Unit of Environmental Chemistry and Membrane Processes). Specially designed and constructed laboratory stand was used (Fig. 5–7), with external water bath providing constant and adjustable process temperature (here 38ºC). Three glass laboratory-size (working volumes 1 dm^3) thermostated bioreactors from the stand were applied – two filled with wastelard (10.0 g) together with starving bacteria strains (inoculum) and one for determination of intrinsic inoculum contribution in the overall biogas production (only inoculum – without lard load). Model substrate (lard) representing commonly used animal fat was initially disintegrated and premixed with inoculum to obtain possibly homogeneous suspension.

Fig. 5. The laboratory-scale system for measurement of biogas generation potential of fat wastes and appropriate process kinetics (photo: Jan Cebula)

Fig. 6. The reactors for the research of anaerobic fermentation course during fat wastes processing (photo: Jan Cebula)

Fig. 7. Laboratory bioeactor for the measurement of methane fermentation process course(photo: Jan Cebula)

Anaerobic fermentation course. The raw experimental data presenting directly batch methane fermentation of waste lard were acquisited manually by periodical observation of current total volume of produced biogas in each fermentor in strictly defined time intervals. The intrinsic inoculum contribution to overall biogas production in each bioreactor (comparative tests in separated bioreactor – in the same process conditions) turned out to be so small, that it could be neglected in proper data trends interpretation. The raw data collected, recalculated per 1 kg of dry mass, were then fitted with modified 3-parameter kinetic Gompertz model (1) [25]:

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

matching to the characteristic time-course of batch anaerobic fermentation (Fig. 8), which three adjustable parameters: $H_{\max}$, $R_{\max}$ and λ, of the precisely defined physical sense:

H – cumulative volume of biogas generated from the process beginning up to defined time t, dm^3/kg of dry mass (dm^3/kg d.m.);

H_{max} – maximally attainable H (theoretical asymptote of Eq. (1)), dm^3/kg d.m.;

R_{max} – maximum biogas production rate, dm^3/kg d.m./h;

λ – duration of lag phase period (bacterial strains adaptation to a given substrate in a given environment), h;

t – batch process time, h.

The parameter values resulting from nonlinear regression procedures are presented in Table.

Kinetic characterization of the batch anaerobic fermentation process of waste lardin laboratory conditions (38 °C) – experimental data elaborated with modified 3-parameter Gompertz model

No	Parameter	Run 1	Run 2	Mean
1	Maximally attainable cumulative biogas volume, Hmax , dm3/kg d.m.	622.19	720.13	668.84
2	Maximum biogas production rate, Rmax , dm3/kg d.m./h	1.067	1.082	1.074
3	Lag phase period, λ, h	246.71	234.81	240.71
Correlation coefficient R2		0.999	0.999	0.999

Based on the kinetic data presented in Table one is able to make short characteristics of anaerobic fermentation of the waste lard. Process will start after relatively long incubation time (ca. 235–247 h, mean 241 h). It is about 10 days, thus from technological point of view some systems of several bioreactors should be considered. In such a system, to avoid decrease in productivity, the reactors should work alternately. For comparison, incubation period for potato wastes varies from 2.88 h (mean for fried chips) up to 47.67 h (mean for potato flour) [26]. However, batch methane fermentation of waste lard is clearly one-stage process (see Fig. 8), contrary to various potato wastes where two or even three distinctly visible stages are observed.

It is important in process technology since fermentation progress can be easily controlled and unequivocally interpreted. The maximum biogas production rate varies from 1.067 to 1.082 dm^3/kg d.m./h, with mean value 1.074 dm^3/kg d.m./h. This value stabilizes within the 350–550 h time window. Methane content in such produced biogas varied from 68,8 to 72,4 with mean level of 70,6 thus from 1 Mg of dry mass (directly mass of waste lard) one is able to obtain 0,758 m^3 of pure methane per hour (assuming, however, operation with possible maximal production rate, usually only in the middle of the batch cycle). Its energetic value is 27,06 MJ/m^3 The maximally attainable cumulative biogas volume varies from ca. 622 to ca. 720 dm^3/kg d.m, with mean level 669 dm^3/kg d.m.

From 1 Mg of waste lard after utilization via fermentation process it is thus possible to produce 622–720 m^3 of good quality biogas instead of troublesome biowaste deposit. Considering the fact, that such relatively large maximal unit production is obtained after one stage, waste lard representing animal fat can be considered as promising raw material for energetic utilization. In case of potatoes corresponding indicator value (after first process stage – for direct comparison) varied from 127.54 dm^3/kg d.m (mean for potato chips) up to 629.58 dm^3/kg d.m (mean for potato peelings) [26]. However, comprehensive economic analysis should consider further possibilities of upgrading this value during second or even third stage. Nevertheless, the overall batch fermentation process time, several lag periods and disadvantageous modification of the process rate in consecutive stages (later significant devaluation of R_{max}) can be important factors in decision about eventual process termination after first, the most effective stage.

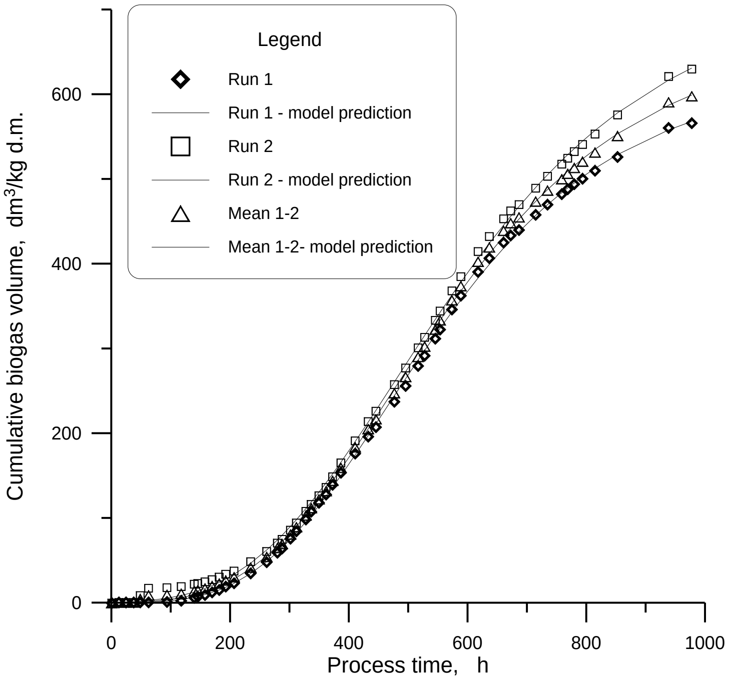


Fig. 8. Graphical representation of the waste lardmethane fermentaton process progress

Conclusions

Based on the research done one can draw the following conclusions and generalizations:

1. Methane fermentation of the waste fat and biomass rich in fats is possible and economical both in fermentation chambers and using the aerobic-anaerobic-aerobic system.
2. Methane fermentation of the biomass containing wastes with various fats seems to be promising technological method of waste lard utilization, since relatively large amount of high methane content biogas with very low hydrogen sulfide concentration is produced.
3. From 1 Mg of waste lard after utilization via anaerobic fermentation process it is possible to produce 622–720 m^3 of good quality biogas instead of troublesome biowaste deposit.
4. Additional research is needed to make more thorough insight into process conditions (including different bacteria strains bioefficiency), identify internal process feedbacks and check their applicability towards optimal process control.

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ВИРОБНИЦТВО БІОГАЗУ З ВІДХОДІВ ТВАРИННИХ ЖИРІВ

Я. Бохджієвіч, К. Піотровський, П. Сакієвіч, Я. Цебуля

Анотація. *Подано результати дослідження, що стосуються виробництва біогазу з відходів свинячого сала. Під час приготування різних смажених страв з використанням свинячого сала або рослинних жирів спостерігається зміна складу жирів. Вони зазнають суттєвих хімічних перетворень у більш чи менш шкідливі продукти. Синтезовані токсичні речовини, розчинені в жирах, стають більше не придатними для вживання в їжу або подальшого використання, тому необхідно зробити безпечним їх використання. Відходи жиру після виробництва смаженої картоплі, пончиків, смаженого м'яса тощо, однак, розглядається як приваблива сировина для виробництва біогазу. Лабораторний аналіз анаеробного процесу ферментації стічного тваринного сала передбачає, що його енергетичне використання може бути перспективним джерелом поновлюваної енергії. З 1 Мг відходів свинячого сала можна виробляти за анаеробної ферментації СА 620 720 м3 біогазу високої якості з максимальною швидкістю в межах від 1,067 до 1.082 дм3/ кг/год.*

Ключові слова: *відходи, свинячий жир, тваринний жир, біогаз, утилізація біовідходів, анаеробна кінетика бродіння, модифікована модель Гомпертца*

ПРОИЗВОДСТВО БИОГАЗА ИЗ ОТХОДОВ ЖИВОТНЫХ ЖИРОВ

Я. Бохджиевич, К. Пиотровский, П. Сакиевич, Я. Цебуля

Аннотация. *Представлены результаты исследования, касающиеся производства биогаза из отходов свиного сала. Во время приготовления различных жареных блюд с использованием свиного сала или растительных жиров, наблюдается изменение состава жиров. Они претерпевают существенные химические превращения в более или менее вредные продукты. Синтезированные токсичные вещества, растворенные в жирах, становятся больше не пригодными для употребления в пищу или дальнейшего использования, поэтому необходимо сделать безопасным их использование. Отходы жира после производства жареного картофеля, пончиков, жареного мяса и т.д., однако, рассматриваются в качестве привлекательного сырья для производства биогаза. Лабораторный анализ анаэробного процесса ферментации сточного животного сала предполагает, что его энергетическое использование может быть перспективным источником возобновляемой энергии. С 1 Мг отходов свиного сала можно производить в анаэробной ферментации CA 620-720 м3 биогаза хорошего качества с максимальной скоростью в пределах от 1,067 до 1.082 дм3/кг/час.*

Ключевые слова: ***отходы, свиной жир, животный жир, биогаз, утилизация биоотходов, анаэробная кинетика брожения, модифицированная модель Гомпертца.***