Opponent's Report

Author of the doctoral thesis: Samuel Emebu, MSc

Title of the doctoral thesis: The Mathematical Modelling of Waste Fats Treatment into Biogas

Supervisor: doc. Ing. Marek Kubalčík, Ph.D.

Opponent: doc. Ing. Pavel Hrnčiřík, Ph.D.

The presented work deals with a highly current topic of the mathematical modelling of waste fats treatment into biogas, very relevant within the context of climate change and recent global energy crisis. A significant part of the initial sections of the submitted text consists of an extremely detailed and in-depth treatment of an overview study of mathematical modelling of this type of complex processes. The subsequent theoretical framework deals with the development of a complex mathematical model of the selected model process in the form of a single-step-degradation model (SSDM). The resulting model not only deals with the main parts of the process, such as hydrolysis of lipid, mass transfer, heat transfer, biochemical stage and pH, but also models the effect of temperature and pressure on the microbial activity, physicochemical and thermodynamic parameters. In the final section of the work, the results of selected simulated scenarios as well as experimental tests performed within this study are presented and discussed. The presented results confirm the suitability of the developed mathematical model for describing the process of anaerobic digestion of waste fats into biogas.

The scientific methods and techniques used within the presented doctoral thesis are at high level and fully correspond with the outlined aims and objectives. Also, in terms of formal requirements the submitted thesis satisfies the usual criteria associated with this type of scientific works. In accordance with the above mentioned, I hereby **RECOMMEND** the doctoral thesis submitted by the doctoral student Mr Samuel Emebu, MSc for the defense.

Comments and topics for discussion within the defense of work:

1. Page 30 – in what range can the basic biokinetic parameters like average specific growth and death rate vary depending on the possible sources of activated sludge and how sensitive is the overall mathematical model with respect to these microbe-related parameters?
2. Table 8.1. – these average properties of sludge samples are based on how many measurements? What is their variance?
3. Table 8.2 – the initial concentration of microbes and their molecular weight are parameters that are quite difficult to determine precisely. How sensitive is the resulting mathematical model of the process and its biogas production predictions to possible uncertainties related to these parameters?
4. A.14 and Table A.4 – what is the meaning of "hypothetical" in relation to the data used for the calculation of maximum specific growth rate of microbes? How was this data obtained?

Prague, 1st November 2023 doc. Ing. Pavel Hrnčiřík, Ph.D.

Opposite opinion.

Work: The Mathematical Modeling of Waste Fats Treatment into Biogas.

Author: Ing. Samuel Emedu.

Opponent: Ing. Prof. Karel Kolomazník DrSc., DHD.

The topic of the dissertation: "The Mathematical Modeling of Waste Fats Treatment into Biogas"

Theses "The Mathematical Modeling of Waste Fats Treatment into Biogas"

of engineer Samuel Emeda is current and necessary. Its need is determined by the probability of the depletion of natural fossil fuel reserves and their replenishment today and replacement by renewable fuels in the future. Actuality consists in researching the mechanism of production of renewable fuels from the continuous production of suitable bio raw materials. The chapter Current state of issues - Research overview is intended to present an overview of the current state of the problem in connection with the topic of the dissertation, i.e. "The Mathematical Modeling of Waste Fats Treatment into Biogas." However, the reality is different. The first paragraph of the mentioned chapter describes the advantages of biogas production from sludge and oils, which could be mentioned in the introduction. The second paragraph describes the chemistry of anaerobic digestion rather than a specific mathematical model. Only at the end of chapter 2.1 is it stated that the kinetic equations of anaerobic digestion can be described by a first-order mechanism. Overall, it can be stated that in the mentioned chapter there is little connection with the topic of the dissertation. However, I am missing a chapter on the evaluation of the current state in connection with the topic of the dissertation. It would show what was solved, what should be solved and what will be solved in the dissertation. This would give clear objectives of the dissertation. Implicitly, the above-mentioned shortcomings are eliminated in the next text of the dissertation. Thermodynamic and kinetic situations for ongoing complex anaerobic reactions are described in detail, accompanied by detailed citations to published professional articles. I consider this part to be very beneficial, both in terms of theory and application for industrial practice. For further additions, especially for planned publications, I would recommend using the established theoretical and experimental results on the complex

kinetics of simultaneous reactions, which in the simple case are described by a vector differential equation, where the individual components of the vector correspond to the first-order mechanism. Next, I present selected formal comments or questions.
p.15 In what form is nitrogen with a concentration of 0-5000 ppm?

In Table 4.3 p.16 Is nitrogen in the form of ammonia?

p.18 capture 5 Control according to the mathematical model is influenced by knowledge of the mechanism of the controlled process.

p.19 capture 5 What does the term anaerobic oxidation mean?

p.20 table 6.1 The mentioned models are not based on the estimation of the real mechanism of the anaerobic digestion process, as the author of the dissertation correctly states, therefore they cannot be used for data extrapolation, but only for interpolation. This makes their use for management problematic, which can be said about other following models, however complexly they are described in the following pages 22 – 25.

p.27 figure 7.2 The presented bioreactor is demanding on the sealing of joints. Why wasn't a volumetric burette used directly to measure the rate of biogas evolution?

p.27 equation 7.1a for V the subscript R is missing.

Balance equation 27 – 34p. they are based on the fundamental law of conservation of mass and are the indisputable basis for the following mathematical models. Their use is therefore essential.

p.35 equation 7.11a applies to ideal gases.

p.36, 37 are equations 7.12e and 7.13c valid for free evaporation? That is, without the convective influence of external mass transfer?

p.37 equation 7.14a Henry's law normally describes the solubility of gases, which is finally explained in the following text.

p.37 equation 7.14a is a general equation for mass transfer from the surface of the liquid phase, where (KLa)j is mass transfer coefficient which can be dependent on Renoylds criterion.

p.40 equation is the γLj surface tension?

p.42 is the equation of (7.17a) electroneutral?

p.45 equation 7.13 instead of temperature distribution better (cleaner) in modeling energy – model isothermal.

p.45 – 49 As was the case with mass balances, enthalpy balances are based on the general principle of conservation of energy and are part of every kinetic model.

p.49 – 52 capture 7.17 describes heat transfer (internal transfer, conduction, external transfer). I believe that due to the thermal properties of the material of the bioreactor wall (glass), the main resistance is given by heat transport through the glass wall of the reactor, which greatly simplifies the quantitative description of heat losses.

p.56 equation 7.3. What is the advantage of using the Caussion model for the temperature dependence of the rate constant over the Arrhenius model ($k = \exp(-E/RT)$)?

p.58 capture 9.1 I did not find the experimental data given in table A.3 in the dissertation.

p.59 – 79 The influence of pressure, pH, and temperature is presented on the indicated pages on the anaerobic rate and is expressed by changing the kinetic parameters of the corresponding quantitative relationships.

The given notes are in most cases of a formal nature and can be taken into account in planned further publications. They do not detract from the otherwise excellent standard of the dissertation, which is currently very relevant and needed.

Dissertation thesis of Ing. I recommend Samuel Emedu "The Mathematical Modeling of Waste Fats Treatment into Biogas" for the defense.

In Zlín October 26, 2023

Prof.Ing. Karel Kolomazník DrSc., DHD.

VYSOKÁ ŠKOLA CHEMICKO-TECHNOLOGICKÁ V PRAZE
Fakulta chemicko-inženýrská
Ústav fyzikální chemie

Oponentský posudek disertační práce „Matematické modelování zpracování odpadních tuků na bioplyn" Ing. Samuela Emebu.

Review of the doctoral thesis "The Mathematical Modelling of Waste Fats Treatment into Biogas" by Ing. Samuel Emebu.

The thesis is devoted to the actual topic of biogas production modelling, which contributes the field of the engineering optimisation of the anaerobic digestion and, in general, the desirable transfer to the low carbon economy. The aims, as listed in section 3 in the work, were fulfilled. Regarding the point 8 of the Aims, it is not clear to me if the SSDM model was compared to experimental data as other models than that were used in section 9.1. The main contribution is in the simulation of the relevant regimes of operation – case studies further in section 9.

The main focus of the work is on the elaboration of the SSDM model and simulation. In my opinion, novel experimental data are not abundant, the models are described with brevity and with the provision of the references to the related literature. The work is burdened by formal issues (see below), many of which are unexpected for an author who has knowledge of the Latex system (CV, page 122). The publication activity of the author is adequate and related to the topic of this Thesis.

In conclusion, I certify that I personally evaluated this doctoral thesis and I have no reservations in my recommendation that it be defended.

In Prague, 8. 11. 2023

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Assoc. Prof. Ing. Ondřej Vopička, Ph.D.

Suggested questions for the PhD defence ceremony:

1) In section 7.9, characteristics of gas bubbles are modelled, while interfacial tension was correlated using literature data from the literature. As literature data are commonly reported for water-gas pairs, deviations can be expected for the complex media containing amphiphilic compounds, such as lipids. Could the author compare the interfacial tension and density (point 6 below) for pure water and for the studied media?

2) In section 8.7, the author states "FTIR could only be used to measure the methane and carbon dioxide content", while only the band of methane is specified (3002-3024 cm^{-1}). Could the author mention which band(s) was used for the quantification of CO2? Did the analysis providing only information on the CO2 and CH4 contents in the produced gas suffice for the models, which predict also concentrations of other gases in the product stream? (e.g. Figure 9.34). I have found no experimental data (by the author) on the gas production, while other relevant experimental results appear in section 9.1.

3) What I am concerned about are unusual units of some quantities, such as "R = 8314 pa.kgmol-1. k^{-1}" on page 37, or "average molecular volume of water, v_{H2O}(m3.$kgmol^{-1}$)". In the literature [171], from which the model of moisture content was taken, the more common units were used: "V_{H2O}, in m^3/mol" and "8314 (m^3.MPa)/(mol.K)". Besides that, two symbols appear to be used for the one quantity, see "molar volume for water ϱw" on page 39.

Comments and remarks, which do not have to be all addressed during the ceremony:

4) In section 4, the author provides an overview on the composition and calorific value of biogas and its constituents. The definition of the calorific value used by the author is unclear to me. Is it the Higher heating value (with liquid water as product) or the Lower heating value (with water vapour as product)? The value is also measured per cubic meter, while the conditions (temperature and pressure) are not explicitly mentioned. Please see also the contradiction resulting presumably from the from the loosely defined calorific value: "The energy value of pure methane is about 35 $MJ.m^{-3}$" (on page 15) and "Calorific value, $MJ.m^{-3}$, 37.7" in Table 4.2.

5) In Table 4.4, "Energy density, $MJ.m^{-3}$" is compared for three grades of biogas, ethanol, and biodiesel. In my opinion, it should be noted explicitly which materials are in the liquid state.

6) In equation 7.15g, another type of correlation than in 7.15h, 7.15i was used without comment. Which model was used for the gas density calculation as used in 7.15g? Which value(s) was used for the liquid density (pure water or real media)? With this regard, other data for methane – water system are available, and presumably enable to use the same pattern of the model as in 7.15h, 7.15i: W. Sachs, V. Meyn, Colloids and Surfaces A: Physicochemical and Engineering Aspects 94 (1995) 291-301.

7) In Table 4.2, wrong critical temperature for CO2 (not minus). Why critical temperature of H2 is not mentioned? Why is the critical temperature of methane set identical to that of biogas (60% CH4 & 40% CO2)?

8) In section 5, I would expect at least a brief elaboration on the involved strains. However, reference to relevant literature is given.

9) Frequently, units and the multiplying constants are written in the Thesis without care about the use of capital letters. For example, megapascal is abbreviated as "Mpa" in Table 4.2. Similarly, symbols of

kelvin, kilojoule, and kilogram do not match multiple times in the work, for instance "The thermal conductivity, $\mathcal{K}$Wv ($W.m^{-1},k^{-1}$)," and "CPWv ($J.Kg^{-1}.K^{-1}$)" in section A.10, "$76.1KJ.mol^{-1}$" in Equation 5.4. One also finds: "R = 8314 $pa.kgmol^{-1}.\ k^{-1}$" on page 37, "specific heat capacity ($J.Kg^{-1}.K^{-1}$)" in section A1, "pj* (pa)" on page 39.

10) In 7.13a, constant 0.76190042 is stated while 761900.42 is in the model (17 as in ref. [171]). I assume that this conversion reflects the use of other water content units than in [171]. I would expect a comment on units.

11) In section A.12, the author states "respectively given in Equation (5.15h) – (5.15i) were deduced". This is a misprinting as the reference should be to Eqns. (7.15h) – (7.15i).

12) In Figure 9.8 (and in other figures), properties of single-component bubbles are plotted. Do single-gas bubbles occur in the real systems or is this a model prediction that needs to be interpreted?

13) In A.15, Equation A.39 is $pi=\Sigma xj.pi$. It seems that pi,j rather than pi should be in the sum. Do symbols in this rule adhere to the list of symbols?

14) In Table 7.2, one reads "Acetate, AcH". On page 42, one reads "[Ac^-] is the concentration of acetic acid". In my opinion, more care should be given to the use of symbols of chemicals. Besides that, the common symbol for acetate is OAc or AcO, while Ac is a common symbol for acetyl.

15) The statement "Biogas is about five times less dense than air" on page 15 does not appear to be realistic. In the same sentence, the author stated "flame temperature of 870 °C and burns with clear blue flame". Although the value seem to be realistic, the flame temperature is generally influenced by a number of factors (I would expect a range rather than a fixed value if conditions, such as fuel to air ratio, are not specified).

16) On page 11, the author stated "Its energy yield per square meter of feedstock". I assume per cubic meter.

17) Some equations are typeset in blue font (e.g. 7.15k), some not (e.g. 7.15l), the purpose is unclear to me. Besides that, most (math) variables are typeset in a normal font, while slanted font is common for this purpose (for example in the Latex system mentioned in the author's CV).

18) Figure A.1 d: It is hard to see in the print as well as in the zoomed pdf that the factor is 10^4.

Formal issues:

19) Very long sentence (6 lines) on page 11: "Furthermore, considering the earlier highlighted…".

20) On page 11, abbreviation AD first is used but not defined in the main text (defined in Abstract).

21) On page 13, the sentence "Although most literature highlights the kinetic of hydrolysis at constant temperature but has not mathematically quantified its effect." would deserve editing. This is also the case of the sentence "While the multi-step dynamic model could be modelled as, a single-step-degradation model (SSDM), two-step-degradation model (TSDM), and multi-step-degradation model (MSDM) [68]." on page 21.

22) On page 18, there is "etc [101]" (missing point).

23) On page 81, there is an unfinished sentence "Furthermore, unlike the ADM1 or other multi-step dynamic models."

23) Missing letter on page 51: "for lamina (Re < 2300)".