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SCUOLA DI INGEGNERIA INDUSTRIALE E DELL'INFORMAZIONE

EXECUTIVE SUMMARY OF THE THESIS

A data-driven model for feedstock blending optimization in anaerobic co-digestion scenarios

TESI MAGISTRALE IN CHEMICAL ENGINEERING – INGEGNERIA CHIMICA

AUTHOR: ALESSIA GORACCI

ADVISOR: GIULIA LUISA BOZZANO

CO-ADVISOR: FEDERICO MORETTA

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1. Introduction

Anaerobic digestion (AD) consists of the spontaneous degradation of substrates through anaerobic bacteria, that in absence of oxygen turn the initial matter into biogas – composed mainly of methane (50-70%) and carbon dioxide (30-50%) – and a liquid-solid residue called digestate. At industrial level, the digestion can be carried out both through a discontinuous and continuous layout, and the efficiency of the process highly depend on the operating conditions (e.g., temperature, total solids (TS, % w/w) content) and on the nature of the feedstock. This project deals with the optimization of the composition of the feedstock of anaerobic digesters.

It has been demonstrated that the AD of a single kind of substrate (e.g., animal manure, agro-industrial and organic waste types, sewage sludge) might lead to low methane yields due to an inappropriate composition, caused by the lack of some nutrients or non-optimal parameters. To improve methane yield, anaerobic co-digestion (AcoD) can be exploited, which consists of the simultaneous digestion of multiple substrates that possibly show complementary characteristics, and then allows to obtain optimal feeding conditions [1]. This way, methane yield and process stability can be significantly improved, and synergistic effects may be observed too. On the other hand, an improper choice of co-substrates could lead to a system imbalance and create antagonistic effects.

The aim of the project, therefore, is to create a model able to predict the best blending conditions to maximize the methane yield of the co-digestion.

2. Feedstock Parameters

The first part of the project consisted of accurate bibliographic research aimed at identifying the most characterizing parameters of AD raw materials. Among all the parameters, the most relevant ones – that have most been used during the building phase of the model – are the C/N ratio and the Biodegradability (BD) of the substrates.

2.1. C/N ratio

The ratio between the organic carbon and nitrogen content is a commonly used parameter to characterize feedstock nutrients. To obtain high methane yields, it has been demonstrated that the C/N should be comprised in a range between 20 and 40: below this range the degradation causes an increase in ammonia concentration that could inhibit the digestion process by microbial growth impediment; on the other hand, above this range, the substrate results rich in carbon sources, leading to the production of high concentrations of VFAs, which are another cause of inhibition due to bacteria deactivation [1].

2.2. Biodegradability (BD)

This parameter represents the degradable fraction of the substrate: indeed, the organic fraction – that could be potentially degraded in ideal conditions, expressed as percentage of volatile solids (VS, %TS w/w) – may be composed both of readily degradable components such as simple carbohydrates, proteins and lipids, and of hardly degradable compounds, that are the lignocellulosic components. In literature, many definitions of this parameter can be found, among which it was decided to use the one shown in Equation 2.1.

$$BD = \frac{EBMP}{TBMP} \tag{2.1}$$

The $TBMP$ (measured in mL/g_{VS}) is the Theoretical Biomethane Potential, that represents theoretical methane yield that could be achieved if the organic matter would be completely degraded, depending on its elemental composition. Supposing to express the organic matter with the chemical formula $C_cH_hO_oN_nS_s$, the $TBMP$ is generally calculated through a modified Buswell formula [2], reported in Equation 2.2.

$$TBMP = \frac{\left(\frac{c}{2}+\frac{h}{8}-\frac{o}{4}-\frac{3n}{8}-\frac{s}{4}\right)\cdot 22415}{12c+h+16o+14n+32s} \tag{2.2}$$

The $EBMP$ (mL/g_{VS}) is instead the Experimental Biomethane Potential, which is the cumulative methane yield obtained in lab-scale batch tests – namely *BMP tests* – performed at controlled operating conditions (generally, with TS of 5-10% and temperature of 35-37°C). This quantity is always lower than the $TBMP$, since the latter does not consider the non-degradable fraction of the substrates, being an ideal parameter. Therefore, BD is comprised between 0 and 1, and represents the degree of degradability of the organic matter contained in the substrate.

2.3. Other Parameters

Secondary parameters that have been considered during the data collection are the TS, VS, and the content of the main macro-nutrients – i.e., lipids, proteins, sugars, starch, easily-degradable carbohydrates, cellulose, hemicellulose, lignin, and ash (%TS w/w).

3. Previous Studies

Numerous experimental studies have been carried out to calculate the optimal blending conditions of mixtures of substrates by performing BMP tests using design of experiments techniques such as Central Composite Design associated with Response Surface Methodology. However, the results that are obtained from this kind of experimentations are not general and can be applied only on the analyzed mixture. In addition, they are time-consuming and require the use of analytical techniques.

On the other hand, some attempts to build models able to predict the optimal feedstock blending have been done in the past: in particular, a control model based on a linear programming [3] and an optimization based on an ant-colony approach [4] have been proposed. However, they are both intended to be applied as on-line control systems and involve the measurement of hardly measurable variables using analytical techniques. The purpose of this work, instead, is the development of an easy-to-use and quick tool that with few, simple inputs can estimate with good precision the optimal blending ratios of mixtures of substrates, aiming at supporting industrial realities with decision-making processes related to the feedstock management.

4. Database Construction

The large number of possible raw materials and the high variability of their composition depending on their source reflects the high complexity of the problem. Therefore, a database was created, as shown in Figure 4.1, collecting data about a large number of substrates and dividing them into four macro-categories. Here, for each substrate, data about the main parameters characterizing them – TS, VS, C/N ratio, lipids, proteins, sugars, starch, easily degradable carbohydrates, lignin, cellulose, and hemicellulose content, TBMP, EBMP, BD – were collected from more than eighty scientific articles.

Due to the high variability of the compositions of substrates, even of the same nature, their parameters are characterized by a distribution. Consequently, to obtain general and reliable values for each parameter, an averaging process was carried out, associating to each a standard deviation. The obtained mean values were used to build the *Primary Averaged Database*, that was then used to identify correlations between the parameters by using regression tools.

After that, a *Secondary Averaged Database* was built by calculating general mean values and the

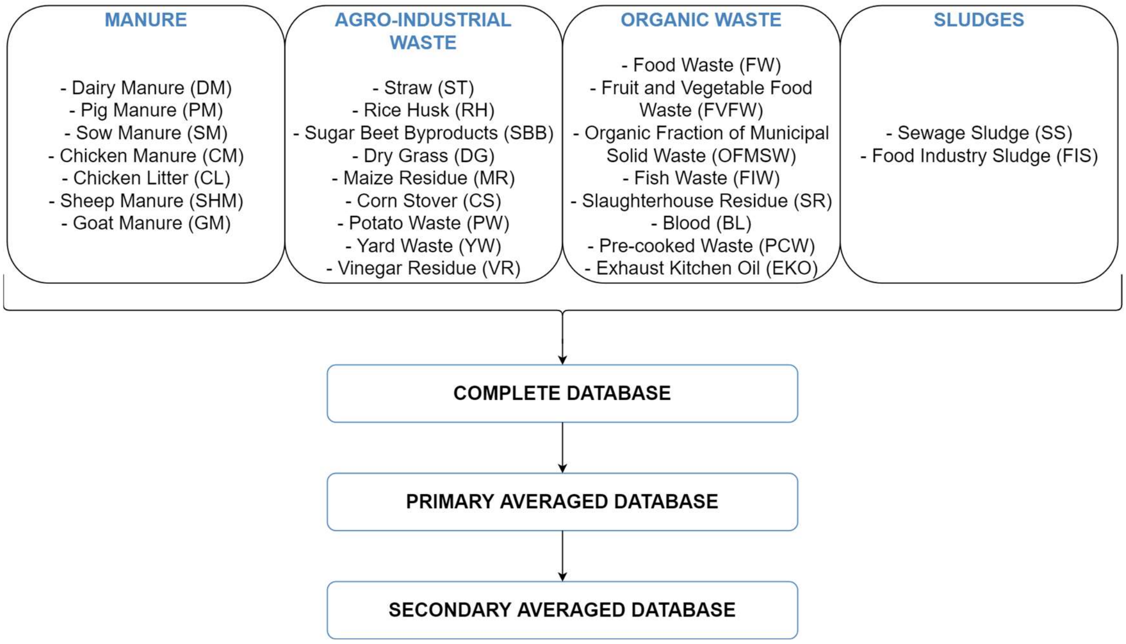


Figure 4.1: Visual representation of the building process of the Complete Database, Primary Averaged Database and Secondary Averaged Database

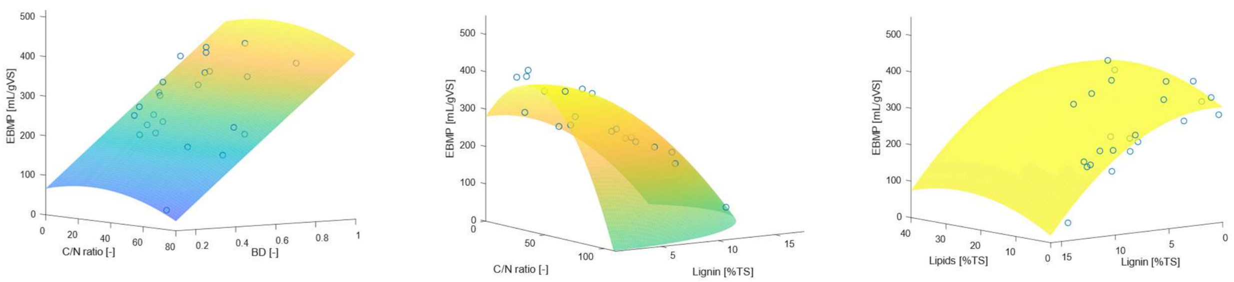
respective standard deviations for each macro-category.

5. Mathematical Correlations

The data of the *Primary Averaged Database* were analyzed to demonstrate the existence of mathematical dependencies of the EBMP on parameters such as the C/N ratio, the BD, and the content of macro-nutrients as lipids and lignin. By using a multi-dimensional regression analysis, it was possible to create two-, three- and four-dimensional relationships between these quantities. For the sake of brevity, only the three-dimensional plots are reported in Figure 5.1. There, it can be observed that clear relationships between the EBMP and substrate parameters exist.
The EBMP generally reaches a maximum as function of the C/N ratio, revealing the optimal range mentioned in Section 2.1; it increases increasing the biodegradability of substrates and decreases at the increase of the lignin content – lignin is indeed the main non-degradable component of substrates. Moreover, the EBMP shows a maximum with respect to the lipids content: in fact, high lipids content might lead to VFA deactivation. The existence of such relationships means that the production of methane strictly depends on the characteristics of substrates and makes it possible to estimate the EBMP of a certain substrate by only knowing the value of some of its parameters.

6. Blending Optimization Model Development

The relationships shown in the previous section allow to estimate the EBMP of a substrate by only knowing some of its parameters. Since the aim of this study is to maximize the methane production of mixtures of substrates, besides the EBMPs of the single substrates, synergistic effects should be considered too. Consequently, an objective



(a) (b) (c)

Figure 5.1: Three-dimensional plots of the EBMP as function of various parameters: points correspond to each Primary Averaged Database substrate; the surfaces represent the regression models.

function representing the co-digestion BMP of a mixture has been defined so that, when maximized, it returns the highest possible BMP and the corresponding feedstock composition in terms of mass fractions of the selected substrates. The algorithm structure is reported in Figure 6.1. The objective function has been defined for the anaerobic co-digestion of two and three substrates (NC=2,3), and the two definitions are reported in Equations 6.1 and 6.2, respectively.

$$f_{obj,NC=} = BMP_{AcoD} = x_1 EBMP_1 + x_2 EBMP_2 + x_1 x_2 BMP_{mix} \tag{6.1}$$

$$f_{obj,NC=3} = BMP_{AcoD} = x_1 EBMP_1 + x_2 EBMP_2 + x_3 EBMP_3 + (x_1 x_2 + x_1 x_3 + x_2 x_3 + x_1 x_2 x_3) BMP_{mix} \tag{6.2}$$

The quantities x_i represent the mass fractions of each substrate *i* in the mixture, therefore Equations 6.1 and 6.2 are built in a way that, if a mono-digestion is performed, the f_{obj} is equal to the $EBMP_i$ of the single substrate. Moreover, interaction terms are added so that the BMP_{AcoD} includes the effects of co-digestion synergies. The interaction terms involve the definition of the quantity named BMP_{mix}. After many tests, BMP_{mix} has been defined by exploiting one of the three-dimensional correlations shown in the previous section, particularly the one between the EBMP and the C/N ratio and BD: BMP_{mix} is indeed defined as the EBMP of a pseudo-single substrate characterized by weighted C/N ratio and BD with respect to the blend composition, as shown in Equations 6.3 and 6.4.

$$\left(\frac{C}{N}\right)_{mix} = \sum_{i=1}^{NC} x_i \left(\frac{C}{N}\right)_i \tag{6.3}$$

$$BD_{mix} = \sum_{i=1}^{NC} x_i BD_i \tag{6.4}$$

The BMP_{mix} is therefore calculated through the expression of the surface of Figure 5.1 (a), that is reported in Equation 6.5, as function of the defined *mix* parameters:

$$BMP_{mix} = \beta_0 + \beta_1 \left(\frac{C}{N}\right)_{mix} + \beta_2 BD_{mix} + \beta_3 \left(\frac{C}{N}\right)_{mix}^2 + \beta_4 BD_{mix}^2 \tag{6.5}$$

The coefficients β_i are obtained through the multi-dimensional regression analysis and are followingly reported.

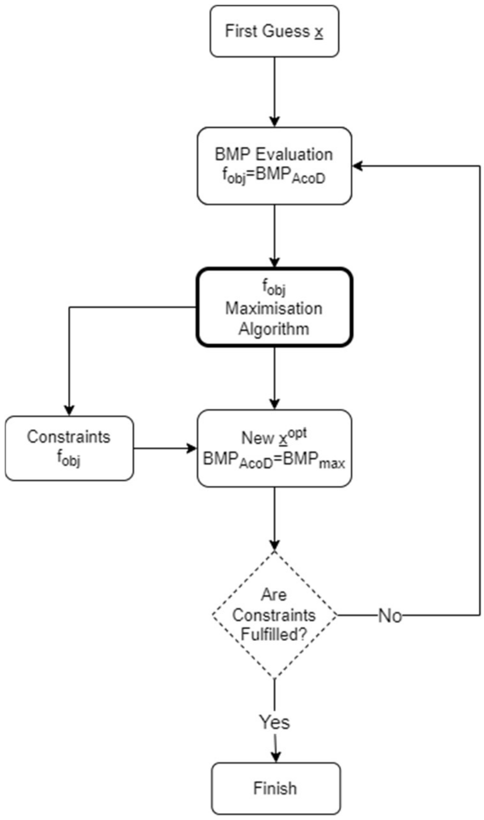


Figure 6.1: Block diagram of the blending optimization algorithm

$$\begin{cases} \beta_0 = 21.6613 \\ \beta_1 = 1.2558 \\ \beta_2 = 445.7076 \\ \beta_3 = -0.0223 \\ \beta_4 = -7.8201 \end{cases} \tag{6.6}$$

Once having chosen two or three substrates about which the EBMP, C/N ratio and BD are known, through the maximization of the f_{obj} by varying the mass fractions x_i, it is possible to calculate the optimal mixture composition. Such maximization must be constrained by Equation 6.7.

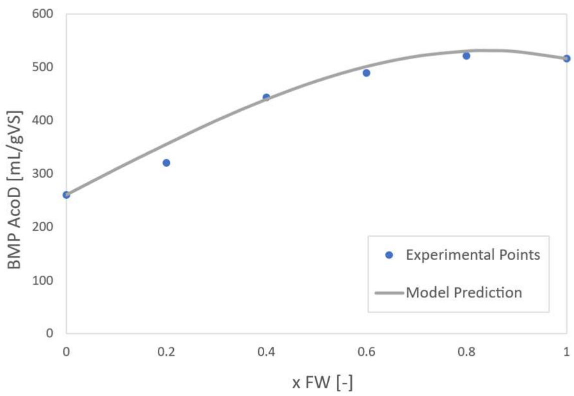
$$\sum_{i=1}^{NC} x_i = 1 \tag{6.7}$$

The quality of this procedure has been validated by comparing the model results with the ones obtained in BMP tests of variable mixtures found in literature. Overall, eight tests were done: five of them involving mixtures of two substrates, and the remaining ones with mixtures of three. Two examples of test results are shown in in Figure 6.2. In Figure 6.2 (a) the comparison between the results of BMP tests performed at different mixing ratios of food waste (FW) and pig manure (PM) [5] and the BMP estimation of the model is reported: there, it can be observed that the BMP estimation is satisfactory at every blending condition with a root mean square error (RMSE) of 15.60 mL/g_{VS}, as well as the estimation of the optimal composition ($x_{FW,opt}$=0.84, $x_{PM,opt}$=0.16). A similar situation is observed in Figure 6.2 (b) where the results of tests on ternary mixtures of dairy manure (DM), pig manure (PM), and straw (ST), are reported [6]. Also in this case the results are reliable both in terms of BMP estimation (RMSE of 20.11 mL/g_{VS}) and optimal composition prediction ($x_{DM,opt}$=0.64, $x_{PM,opt}$=0.27, $x_{ST,opt}$=0.09). The results obtained in these two trials and in the other ones have made it possible to validate the model, confirming its predictions as trustworthy – even though, at times, a BMP over/under-estimation is observed.

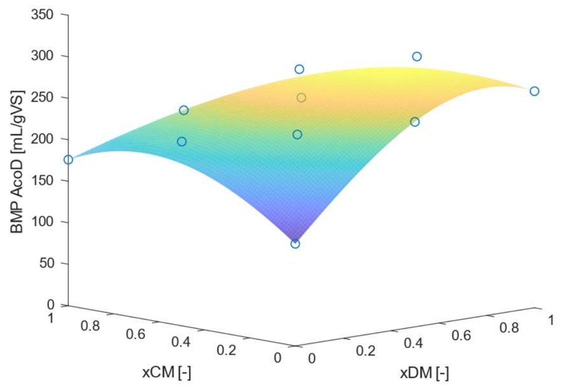
At times, an absence of synergy is observed. Therefore, in those cases another model was built, in which the BMP_{AcoD} is expressed as the weighted average of the EBMPs of the single substrates (Equation 6.8).

$$BMP_{AcoD} = \sum_{i=1}^{NC} x_i \cdot EBMP_i \tag{6.8}$$

This model was validated with two additional tests, however it is currently not possible to automatically predict when this applies.



(a)



(b)

Figure 6.2: (a) Comparison between the experimental BMPs for a variable mixture of FW and PM, and the model results; (b) Comparison between the experimental BMPs for a variable mixture of DM, PM and ST, and the model results.

7. Model Improvements for Industrial Layouts

In case of industrial realities, besides the composition of the optimal mixture in terms of highest methane potential, other issues must be faced, like the real availability of the substrates and the waste storage capability of the plant. Therefore, to consider these additional factors, the model presented in the previous section was improved with new constraints both in case of batch and CSTR-based anaerobic digesters.

7.1. Batch Digesters

In case of batch digesters, when optimizing the feedstock, it must be considered that each substrate has its own availability (in terms of tons per cycle) and that the plant has a certain waste storage capability that determines the minimum quantity of each raw material that has to be disposed in a cycle not to have excessive accumulation.

Supposing to fix the total quantity of substrates that can be loaded into the reactor, named m_{TOT}, it is possible to impose that each substrate load must be comprised between a lower limit, represented by the minimum required consumption, and an upper limit, represented by the maximum availability (Equation 7.1); in addition, the sum of all loads must be m_{TOT} (Equation 7.2). The mass fractions of each substrate can be calculated with Equation 7.3.

$$m_{i,min} \leq m_i \leq m_{i,max} \tag{7.1}$$

$$m_{TOT} = \sum_{i=1}^{NC} m_i \tag{7.2}$$

$$x_i = \frac{m_i}{m_{TOT}} \tag{7.3}$$

The objective function can be then calculated and maximized by varying the substrate loads – instead of their mass fractions. This way the feedstock optimization is performed considering supply chain requirements.

7.2. CSTR Digesters

In case of a CSTR, the modification of the model is analogue to the discontinuous case, except for the fact that instead of massive loads, massive flow rates (expressed in ton/d) are involved. In this case a total massive flow rate $\dot{m}_{TOT}$ must be fixed, and a lower and higher threshold for each flow rate $\dot{m}_i$ can be defined depending on the storage capability and on the availability of substrates, respectively. Equations 7.1, 7.2 and 7.3, therefore, are valid in this case too, and the objective function maximization can be performed by varying the massive flow rates $\dot{m}_i$. This way, optimal flow rates for each substrate, complying with the supply-chain requirements, are obtained.

To validate the CSTR model configuration, an industrial case-study was developed, based on the industrial data shared by Thöni s.r.l. about a 1000 kW biogas plant. By optimizing the received data, an optimized feedstock schedule over the month of January 2022 was calculated using the optimization tool, and the comparison between real and optimized mass flow rates is shown in Figure 7.1.

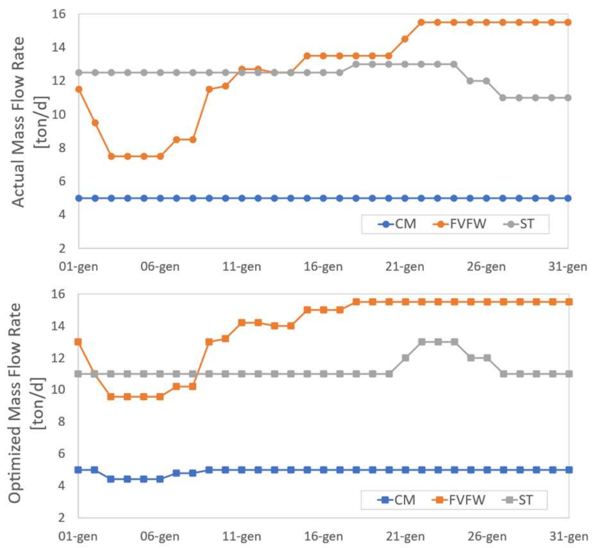


Figure 7.1: Actual mass flow rates and optimized mass flow rates during the month of January 2022

8. Conclusions

The purpose of the project was to develop an optimization tool able to calculate in a trustworthy way the optimal feedstock conditions in different industrial settings. The optimization model was developed starting from a database obtained through the analysis and averaging of data got from more than eighty scientific articles and was first validated by the comparison with batch experimental tests. Then, it was made suitable for applications at industrial level to comply to supply chain issues. The final optimization model demonstrated to yield satisfactory and practical results, and was validated by the comparison with industrial data provided by the companies Rota Guido s.r.l. and Thöni s.r.l.

To obtain even more reliable and flexible results, improvements should be done to the model. Some of the possible improvements are: the addition of information about the localization of the plant, in order to broaden the consideration of supply chain factors; connecting the tool to anaerobic digestion models such as ADM1; the introduction of *correction factors* in the objective function to predict the synergy between substrates; extending the objective function expression to an indefinite number of substrates; validating the model with dedicated experimental tests.

9. Acknowledgments

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