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Modelling of Biomethane Production from Microalgae

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Microalgae are a prospective feedstock for bioenergy due to their higher productivity, adaptable growing environments, and higher lipid/polysaccharide content compared to terrestrial biomass. Anaerobic digestion is a well-established process that can turn microalgae into biogas and offers a high energy return on investment. The ADM1 model, coupled with a pre-treatment step and a full upgrading processing of the biogas, was implemented. Aspen Plus was the software used to display the process of converting biomass to biomethane through anaerobic digestion and biogas purification techniques in order to determine the mass balance and energy requirements. Simulations were compared to experimental data obtained from University of Almeria, Spain of an anaerobic digester fed with Scenedesmus microalgae. For a 5-ha wastewater open raceway pond and a biomass productivity of 20 g/m^2/day, the biomethane had a purity of 94 % using anaerobic digestion accompanied with an enzymatic pre-treatment and amine scrubbing for biogas purification.

1. Introduction

The world is currently having a difficult time keeping up with the rising demand for energy, driven by population growth, urbanization, and industrialization. Fossil fuels have historically been the main source of energy, but their finite supply, growing costs, and detrimental impacts on the environment have driven a shift towards alternative sources of energy (IEA, 2024). Renewable energy is becoming more and more competitive with fossil fuels thanks to economies of scale as well as research and development initiatives. In the context of ambitions to reach net-zero emissions, one of the most attractive biofuels is biogas that may be generated from a variety of terrestrial, renewable bio-based feedstocks. If managed sustainably, it can contribute to the reduction of greenhouse gas emissions and air pollution while serving as a sustainable and renewable source of energy for heat, power, and transportation (Ayala-Parra et al., 2017). Most of this gas is methane (CH_4) and carbon dioxide (CO_2) which can be used for a variety of purposes, including the production of heat and electricity, liquefaction into methanol, compression into vehicle fuel, and purification into pipeline gas (IEA, 2020). As such, the share of biogas used for power and heat will rise to 85 % by 2040 (IEA, 2020).

The production and conversion of these feedstocks could come, however, with concerns related to eutrophication, freshwater resource depletion, food chain disruption, and biodiversity loss. The focus on microalgal biogas production has been heightened to address the drawbacks of first- and second-generation biofuels because it has been determined that such traditional biomass is not completely carbon neutral (Gerado et al., 2015). Microalgae, a prospective feedstock, has numerous benefits over terrestrial plants, including a rapid rate of growth, the capacity to use atmospheric CO_2, and the ability to be grown on non-arable areas using wastewater as a growth medium (Cavinato et al., 2017). Biogas can be obtained from harvested microalgae biomass by a traditional and naturally occurring biological process, namely anaerobic digestion (AD). In AD, several bacterial and archaeal species interact in an oxygen-free environment to biodegrade organic materials into biogas. This method recovers the stored energy from biomass and releases ammonium and phosphate, which can in turn be used as nutrients for microalgae cultivation. Therefore, combining microalgae cultivation with anaerobic digestion offers a viable way to convert solar energy into methane. After AD, the produced biogas

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largely consists of CH_4 (55-70 %) and CO_2 (30-45 %), as well as trace amounts of H_2S (50-2000 ppm), H_2O, and H_2 (Harun et al., 2018).
The aim of this work was to develop a simulation model of microalgal biogas using Aspen Plus software and life cycle thinking as the methodological framework. This integrated method promotes decision-making and optimization of the process ensuring it is scalable and efficient while determining the essential information to model a precise replica of the desired process. Its significance lies in the potential of microalgae as a sustainable energy source, contributing to the reduction of fossil fuel dependence. As a result, the required mass and energy inputs were estimated using mass and energy balances and based on experimental data from the University of Almeria and Aspen plus software for the AD stage to identify upscaled scenarios, a working flowsheet was built in a way that it would be consistent with the actual data collected.

2. Modes and Materials

This work explores a cultivation baseline scenario using wastewater in pilot open raceway ponds at University of Almeria for microalgae growth, eliminating the need for additional nutrients. The process begins with the installation of infrastructure, followed by cultivation in open raceway pond, where wastewater and CO_2 are continuously stirred, compensating for water loss due to evaporation. Harvesting occurs through single-stage membrane filtration, and the permeate is discharged safely. AD involves four steps as shown in

Figure 1: enzymatic pre-treatment to break down cell walls, digestion in a CSTR to produce biogas, upgrading the biogas to biomethane via amino chemical washing, and valorising the digestate by separating it into solid and liquid components for potential fertilizer use and nutrient recycling.

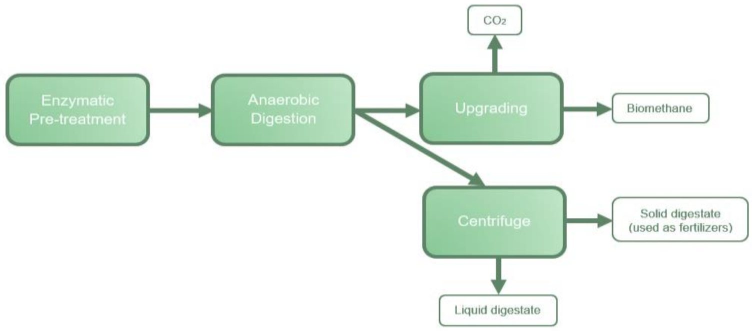

Figure 1: Biomethane Production Flowsheet

2.1 Simulation Model

Most industrial companies are concentrating on process simulation modelling since it is a method to reduce time and financial investments and accurately replicates plant operations. Aspen Plus software was used to model the desired anaerobic digestion process of microalgae and the upgrading part of the biogas.
The first step in the simulation procedure is choosing the property package, in this case NRTL (non-random, two liquid model) was chosen due to its capability to compute activity coefficients and mole fractions, includes vapor and liquid phases, and incorporates polar substrate components. Anaerobic digestion kinetics can be described by a variety of models. Some of these models concentrate on the process's inhibitors, whilst other models describe the AD process. The most fundamental model for AD is known as Anaerobic Digestion Model No. 1 (ADM1) which provides the reaction kinetics of the anaerobic digestion stages and of the temperature.

2.1.1 Scope of application of the model

The developed model for anaerobic digestion and biogas upgrading using ASPEN Plus is versatile and applicable to various scales of biogas production facilities. This flexibility makes it suitable for both small pilot plants and large industrial setups that aids in the design, optimization, and operation of AD systems. It contributes also significantly to the advancement of sustainable biogas production technologies and lays the groundwork for evaluating the economic feasibility of this process.

2.1.2 Microalgae composition

ADM1 model assumes that the substrate fed into the system as a feed will be composed of proteins, carbohydrates, lipids, and inerts. In the case of microalgae, carbohydrates were incorporated as $(C_6H_{12}O_6)_n$, lipids as triolein $(C_{57}H_{104}O_6)$, and proteins as $(C_{4.7}H_{8.7}O_{2.2}N_{1.24}S_{0.02})$.

For the case of proteins, the formula was found based on the amino acid profile of the cultivated microalgae. Table 1 summarizes the microalgae composition which will be introduced as the feedstock in the Aspen model.

Table 1: Microalgae composition

	Raw Scenedesmus (wastewater)	
	Mean	SD
pH	6.4	± 0.1
N-NH_4+ (mg/L)	141.2	± 3.7
C/N	6.3	± 0.1
TCOD (g/L)	27.6	± 2.1
TS (g/L)	16.8	± 1.4
VS (g/L)	15.2	± 1.0
Inert (%)*	9.1	± 0.6
Carbohydrates (%)*	18.1	± 1.6
Proteins (%)*	52.3	± 0.5
Lipids (%)*	20.5	± 1.1

*Percentage calculated based on dry matter content

2.1.3 Reaction list

The precise reactions involved in the AD are added as following the power law of first order in which their kinetic constants are obtained from previous literature studies and showed in Table 2 (Rajendran et al., 2014).

Table 2: Reaction list involved in the digestor

Phase	Number	Compound	Reaction
Hydrolysis	1	Cellulose	$(C_6H_{12}O_6)_n + H_2O \rightarrow n\ C_6H_{12}O_6$
	2	Cellulose	$C_6H_{12}O_6 + H_2O \rightarrow 2\ C_2H_6O + 2CO_2$
	3	Ethanol	$2\ C_2H_6O + CO_2 \rightarrow 2\ C_2H_4O_2 + CH_4$
	4	Triolein	$C_{57}H_{104}O_6 + 3\ H_2O \rightarrow C_3H_8O_3 + 3\ C_{18}H_{34}O_2$
	5	Proteins	Proteins + Water → AA
Amino Acid Degradation	1	Glycine	$C_2H_5NO_2 + H_2 \rightarrow C_2H_4O_2 + NH_3$
	2	Threonine	$C_4H_9NO_3 + H_2 \rightarrow C_2H_4O_2 + 0.5\ C_4H_8O_2 + NH_3$
	3	Histidine	$C_6H_8N_3O_2 + 4\ H_2O + 0.5\ H_2 \rightarrow CH_3NO + C_2H_4O_2 + 0.5\ C_4H_8O_2 + 2\ NH_3 + CO_2$
	4	Arginine	$C_6H_{14}N_4O_2 + 3\ H_2O + H_2 \rightarrow 0.5\ C_3H_6O_2 + 0.5\ C_2H_4O_2 + 0.5\ C_5H_{10}O_2 + 4\ NH_3 + CO_2$
	5	Proline	$C_5H_9NO_2 + H_2O + H_2 \rightarrow 0.5\ C_2H_4O_2 + 0.5\ C_3H_6O_2 + 0.5\ C_5H_{10}O_2 + NH_3$
	6	Methionine	$C_5H_{11}NO_2S + 2\ H_2 \rightarrow C_3H_6O_2 + H_2 + CH_4S + NH_3 + CO_2$
	7	Serine	$C_3H_7NO_3 + H_2O \rightarrow C_2H_4O_2 + NH_3 + CO_2 + H_2$
	8	Threonine	$C_4H_9NO_3 + H_2O \rightarrow C_3H_6O_2 + NH_3 + CO_2 + H_2$
	9	Aspartic Acid	$C_4H_7NO_4 + 2\ H_2O \rightarrow C_2H_4O_2 + NH_3 + 2\ CO_2 + 2\ H_2$
	10	Glutamic Acid	$C_5H_9NO_4 + H_2O \rightarrow C_2H_4O_2 + 0.5\ C_4H_8O_2 + NH_3 + CO_2$
	11	Glutamic Acid	$C_5H_9NO_4 + 2\ H_2O \rightarrow 2\ C_2H_4O_2 + NH_3 + CO_2 + H_2$
	12	Histidine	$C_6H_8N_3O_2 + 4\ H_2O + 0.5\ H_2 \rightarrow CH_3NO + C_2H_4O_2 + 0.5\ C_4H_8O_2 + 2\ NH_3 + CO_2$
	13	Arginine	$C_6H_{14}N_4O_2 + 6\ H_2O \rightarrow 2\ C_2H_4O_2 + 3\ H_2 + 4\ NH_3 + 2\ CO_2$
	14	Lysine	$C_6H_{14}N_2O_2 + 2\ H_2O \rightarrow C_2H_4O_2 + C_4H_8O_2 + 2\ NH_3$
	15	Leucine	$C_6H_{13}NO_2 + 2\ H_2O \rightarrow C_5H_{10}O_2 + NH_3 + CO_2 + 2\ H_2$
	16	Isoleucine	$C_6H_{13}NO_2 + 2\ H_2O \rightarrow C_5H_{10}O_2 + NH_3 + CO_2 + 2\ H_2$
	17	Valine	$C_5H_{11}NO_2 + 2\ H_2O \rightarrow C_4H_8O_2 + NH_3 + CO_2 + 2\ H_2$
	18	Phenyalanine	$C_9H_{11}NO_2 + 2\ H_2O \rightarrow C_6H_6 + C_2H_4O_2 + NH_3 + CO_2 + H_2$
	19	Tyrosine	$C_9H_{11}NO_3 + 2\ H_2 \rightarrow C_6H_6O + C_2H_4O_2 + NH_3 + CO_2 + H_2$
	20	Glycine	$C_2H_5NO_2 + 0.5\ H_2O \rightarrow 0.75\ C_2H_4O_2 + NH_3 + 0.5\ CO_2$
	21	Alanine	$C_3H_7NO_2 + 2\ H_2O \rightarrow C_2H_4O_2 + NH_3 + CO_2 + 2\ H_2$
	22	Cysteine	$C_3H_6NO_2S + 2\ H_2 \rightarrow C_2H_4O_2 + NH_3 + CO_2 + 0.5\ H_2 + H_2S$
Acidogenesis	1	Dextrose	$C_6H_{12}O_6 + 0.1115\ NH_3 \rightarrow 0.1115\ C_5H_7NO_2 + 0.744\ C_2H_4O_2 + 0.5\ C_3H_6O_2 + 0.4409\ C_4H_8O_2 + 0.6909\ CO_2 + 1.0254\ H_2O$
	2	Glycerol	$C_3H_8O_3 + 0.04071\ NH_3 + 0.0291\ CO_2 + 0.00005\ H_2 \rightarrow 0.04071\ C_5H_7NO_2 + 0.94185\ C_3H_6O_2 + 1.093\ H_2O$

Table 2: Reaction list involved in the digestor (Continued)

Phase	Number	Compound	Reaction
Acetogenesis	1	Oleic Acid	$C_{18}H_{34}O_2 + 15.2396\,H_2O + 0.2501\,CO_2 + 0.1701\,NH_3$ $\rightarrow 0.1701\,C_5H_7NO_2 + 8.6998\,C_2H_4O_2 + 14.4978\,H_2$
	2	Propionic Acid	$C_3H_6O_2 + 0.314336\,H_2O + 0.06198\,NH_3$ $\rightarrow 0.06198\,C_5H_7NO_2 + 0.9345\,C_2H_4O_2$ $+0.660412\,CH_4 + 0.160688\,CO_2 + 0.000552\,H_2$
	3	Isobutyric Acid	$C_4H_8O_2 + 0.8038\,H_2O + 0.0006\,H_2 + 0.0653\,NH_3$ $+0.5543\,CO_2 \rightarrow 0.0653\,C_5H_7NO_2 + 1.8909\,C_2H_4O_2 + 0.446\,CH_4$
	4	Isovaleric Acid	$C_5H_{10}O_2 + 0.8044\,H_2O + 0.0653\,NH_3 + 0.5543\,CO_2$ $\rightarrow 0.0653\,C_5H_7NO_2 + 0.8912\,C_2H_4O_2 + C_3H_6O_2$ $+0.4454\,CH_4 + 0.0006\,H_2$
Methanogenesis	1	Acetic Acid	$C_2H_4O_2 + 0.022\,NH_3$ $\rightarrow 0.022\,C_5H_7NO_2 + 0.945\,CH_4 + 0.066\,H_2O + 0.945\,CO_2$
	2	Hydrogen	$14.4976\,\mathrm{H}_2 + 0.0836\,NH_3 + 3.8334\,CO_2$ $\rightarrow 0.0836\,C_5H_7NO_2 + 3.4154\,CH_4 + 7.4996\,H_2O$

2.1.4 Model description

Figure 2 and 3 show the process flow diagram modelled on Aspen Plus of the whole anaerobic digestion and upgrading stages respectively.

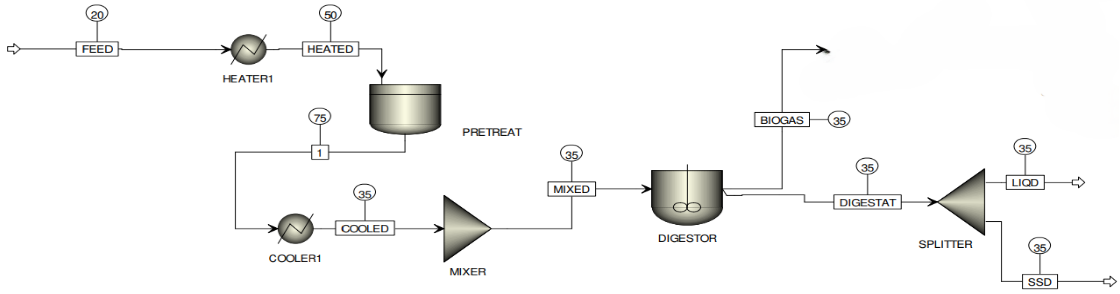

Figure 2: Microalgae AD Plant Simulation

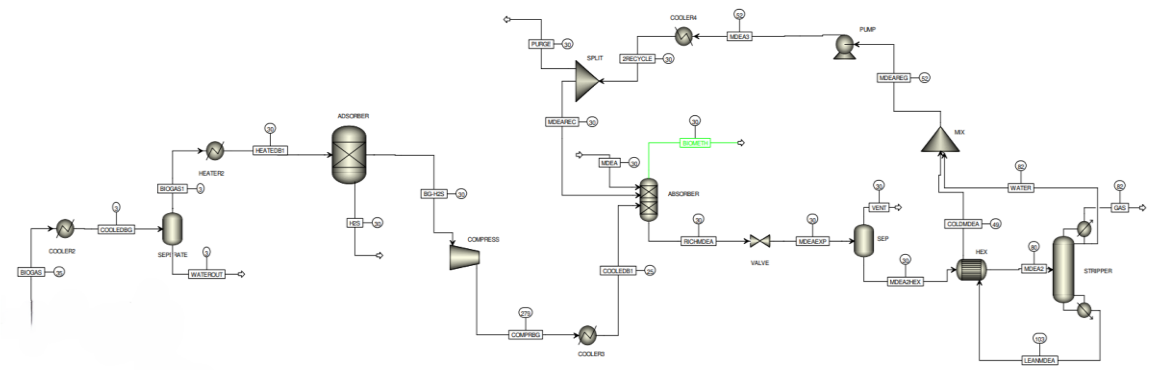

Figure 3: Biogas Upgrading Processing Plant Simulation

Hydrolysis is one of the rate limiting steps in AD, and hence the enzymatic pre-treatment improved its efficiency which was modelled in a batch reactor at atmospheric pressure in the presence of Alcalase (Novozymes, 2015) of quantity 0.2 mL/g algaeDM and a density of 1.08 g/mL that degraded the cell walls' proteins into amino acids. The next step is the anaerobic digestion itself where all reactions of the four phases (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) take place on a kinetic basis (power law) (Table 2). A series of calculator blocks were implemented to compute the rate reactions in the AD in every iteration loop, which are basically written by Fortran code. In total, for glycerol, valeric acid, butyric acid, propionic acid, amino acids, dextrose, oleic acid, methanogenesis, and hydrogen-utilizing processes, eight distinct calculator blocks were utilized. For example, amino acids are transformed into a number of volatile fatty acids (VFA) components after passing through an amino acid calculator block. In order to compute the amount of produced biogas and, consequently, the rate of the reactions, these components pass through multiple VFA calculator blocks, including the valeric acid block and the propionic acid block, followed by the methanogenesis block.

For this step, a CSTR was used to operate in mesophilic conditions (35 °C),1 atm, and an HRT of 18 days. At this point, the AD is completed with two streams existing the reactor. One is the biogas which will be sent to the upgrading process and the other is the digestate which is centrifuged to separate the liquid part from the solid residues that can be used later as a fertilizer.
Once the biogas is obtained, the first stage in the upgrading is drying the biogas, in which it is cooled to 3 °C, and hence, water is drained based on its condensation. The dried biogas must now be desulphurized in which the iron oxide adsorption method is adopted. As a result, an absorber of capacity 150 mg/g adsorbent working under 1 atm and at 30 °C, is used to ensure that the level of hydrogen sulphide in the final product is below 5 ppm so that it can be directly injected into the natural gas grid (Wasajja et al., 2020).
There is still the CO_2 to be removed which is done by the amine washing in which the biogas is compressed to 5 bar and sent to an adsorber of 10 stages is used with aqueous MDEA (45 wt%). At this step, the desired product is obtained which is the biomethane at the top of the column while from the bottom the CO_2 rich MDEA is regenerated using a stripper of 20 stages.

3. Results and Discussion

The main difficulty when building the Aspen Plus AD simulation model is that it needs an analysis of the feed to function properly. Microorganisms are responsible for the anaerobic digesting process but Aspen cannot model their activity. Instead, only the kinetics and reactions that take place during the process are simulated.

3.1 Model Validation

Any proposed simulation model must be validated before it can be widely used and hence replicated under different parameters. This can be achieved by comparing the results produced by experimental setups operating in similar environments with the outcomes anticipated by the model. To verify the model's accuracy, the results from the model were compared with experimental data obtained from partners in Almeria, Spain. This experiment used a 55.5 ml/day of feedstock to be processed in a 1.5 L CSTR reactor with a hydraulic retention time of 18 days at an OLR of 1.5 gCOD/(L.day) which were the conditions of the simulation. The experimental results from this study obtained a CH_4 concentration of 71.25 mol%. Similarly, the Aspen model simulation obtained a CH_4 concentration of 73.4 %. This represents a percentage difference of 2.15 % which allows to conclude that the Aspen Plus model is applicable as the difference between the experimental data from Spain and the Aspen Plus simulation model was minimal.

3.2 Model Upscale and Results

After the model is validated, the purpose behind the simulation is to be able to upscale the production from 55.5 ml/day of feedstock to 67 m^3/day under the same conditions. In this matter, the model was modified and the following results in Table 3 and Table 4 were obtained.

Table 3: Results of the simulation

	Feed	Solid Digestate	Biogas	Biomethane
Mass flowrate (kg/h)	2769.68	1103.75	102.91	50.17
Temperature (℃)	20	35	35	30
Pressure (bar)	1	1	1	5

Table 4: Composition of the obtained biogas and biomethane

Component (mol%)	Biogas	Biomethane
CH_4	73.4	94.09
CO_2	18.4	2.59
H_2O	5.52	0.7
H_2	1.68	2.6
H_2S	214.4 ppm	< 1 ppm

The results are promising in that a biomethane of 94 mol% purity, reduced CO_2 of 2.59 mol%, and low H_2S and H_2O concentration is obtained and meets the specifications to be able to be introduced directly into the natural gas grid for France and Spain. These specifications include a minimum methane content of 90 mol%, CO_2 content less than 3 mol%, and H_2 content below 5 mol%, among other criteria (Marcogaz, 2024).
Hence, the biomethane obtained can be served as an alternative to natural gas. It has a calorific value of 36 MJ/m^3 and hence it was calculated to have an energy output of 73,092.28 MWh.

4. Conclusions

Microalgae show considerable promise as a supplementary energy supply due to their rapid growth, ease of production, and lack of need for fertile agricultural land. Biogas has been promoted as the simplest energy type to produce utilizing microalgae; thus, substantial attempts are being made to demonstrate its efficiency.

This paper highlights the culture and anaerobic digestion of microalgae and determine what information was necessary to model a precise replica using the process modelling software ASPEN Plus. The simulation model covered current research on using microalgae for anaerobic digestion to produce energy. The model included the enzymatic pretreatment to favor hydrolysis. Additionally, it incorporated the anaerobic digestion process as well as the purification of the raw biogas by dehydration, desulphurization, and amine washing to obtain the biomethane. The data gathered from the partners in Almeria, Spain, validated the model, making it suitable for usage as an upscale model up to the desired amount. The simulation results demonstrated an OLR of 1.5 g/L.day and an HRT of 18 days, which achieved a biomethane of 94.1 % purity.

Although microalgae have the potential to produce sustainable amounts of biogas, their conversion efficiency and biogas yield are inferior to those of traditional feedstocks, particularly food wastes. Therefore, co-digestion, integrated biorefinery, and strain-improvement technologies should be given priority in enhancing the conversion of microalgae into biogas. Full research is needed, with a special emphasis on cutting-edge reactor designs that guarantee low HRT and high OLR. The generation of sustainable biofuels using microalgae as a feedstock will expand their applicability in the near future under this biorefinery system. As despite the comprehensive modeling and simulation efforts, the optimization of the enzymatic pre-treatment process requires further investigation to maximize biogas yield and cost-effectiveness. The study also requires a thorough economic feasibility analysis for large-scale implementation, which is crucial for commercial viability Lastly, the variability in microalgae feedstock composition and availability, which can significantly affect the anaerobic digestion process, has to be precisely addressed. Future research should focus on these areas to enhance the robustness and practicality of microalgae-based biogas production.

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Nomenclature

CSTR – continuously stirred tank reactor
HRT – hydraulic retention time
OLR – organic loading rate
C/N – carbon to nitrogen ratio

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