Integral use of aromatic plants: prefeasibility comparison of stand-alone and biorefinery processes using thyme (*Thymus vulgaris*) as base case

Paula Andrea Marín-Valencia[1], Estefanny Carmona-Garcia[1], Jhonny Alejandro Poveda Giraldo[1], Nayda Patricia Arias Duque[2], Carlos Ariel Cardona Alzate[1]

[1]Instituto de Biotecnología y Agroindustria, Departamento de Ingeniería Química, Universidad Nacional de Colombia sede Manizales, Manizales, Colombia
[2]Universidad de Boyacá, Tunja, Colombia
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Presenting author email: pamarinv@unal.edu.co

1. Introduction

Antioxidants are compounds that inhibit or delay onset of oxidation of other molecules, inhibiting the initiation or propagation of oxidative chain reactions [1]. Natural antioxidants may be present in many plants as a defense towards oxidative degradation coming from the environment. Many plants have been considered as potential antioxidant sources, several popular herbs and spices are known to have beneficial effects for human health [2]. Extraction from aromatic plants is widely employed due to the beneficial effects of its components, which are present in a low proportion in the plants.

Thyme (*Thymus vulgaris*) is an aromatic plant, it is native from Western Asia, Central Europe and North Africa, but it is possible to find it as a crop in different parts of the planet, it is cultivated at 1700 meters above sea level. Thyme has stimulating, antispasmodic, antiseptic, healing and antioxidant properties [3]. The chemical applicability of thyme is closely related to the interesting compounds extraction. However, the yield to these compounds is low, indicating that a large part of the plant is remaining [4]. One route of its valorization is through the production of energy from biogas. The biogas production could help to energy recovery in industries and homes, especially in non-interconnected areas, promoting the development of a sustainable and environmentally friendly energy bio-economy [5]–[7].

The aim of this work is to evaluate experimentally the production of essential oil from thyme and the subsequent production of biogas. A conventional extraction was carried out with 60% ethanol at 40°C with constant agitation. Then the solid remaining was subject to an anaerobic digestion at 37°C in order to produce biogas. A simulation of the standalone processes (oil extraction and biogas production) was carried out. Subsequently, a biorefinery approach was proposed in which the processes of oil extraction and biogas production with a cogeneration system (power and heat) were integrated. Last with the purpose of comparing the best route in technical, energy, economic and environmental terms.

2. Materials and methods

2.1. Characterization

Thyme was obtained from Manizales-Colombia 5°03′58″N 75°29′05″O. Raw material was dried at 40ºC to a constant weight. Then, it was milled with an upper vibratory disk mill and sieved to a particle size of 400 μm. Characterization of thyme was performed in terms of moisture, cellulose, hemicellulose, lignin, extractives, ash, total solids (TS) and volatile solids (VS) following standard methods. This chemical characterization, was used as the initial composition of thyme in the simulations.

2.2. Extraction

The antioxidant extract of thyme was obtained by conventional extraction, the samples was disposed in a flask adding ethanol 60% in a 20:1 solvent:solid ratio (%v/w). The procedure was carried out during 3 hours by shaking at constant temperature (40°C) and 150 rpm. Then, the liquid fraction was separated by filtration. The extraction conditions were selected based on literature [8][9].

2.3. Anaerobic digestion

The spent thyme was used for biogas production. The adjustment of digestion medium was performed using as inoculum an activated sludge from a UASB reactor in a coffee factory. For this purpose, the protocol of the international standard VDI 4630 was followed [10]. To adjust the digestion medium, it was necessary to ensure that for each 500 ml of digestion volume, the inoculum should provide between 7.5–10 g of volatile solids. Additionally, a volatile solid ratio of the raw material and the inoculum was maintained less than 0.5. Then, the volume of digestion was completed with tap water. On the other hand, the digestion medium contained a macro and micronutrient described by Angelidaki, 2009 [11]. Afterwards, the pH value was adjusted to 7 with 1 N HCl. Nitrogen was bubbled in the medium for 3 min to ensure anaerobic conditions. Therefore, digestion medium was left under incubation at 37°C for 15 days. The measurement and recording of the biogas produced (concentration) was carried out by a gas analyzer equipment (Gasboard – 3100P portable infrared syngas analyzer).

2.4. Simulation procedure

The process to obtain antioxidant compounds from thyme, and its subsequent use for biogas production was performed in the software Aspen Plus (ASPEN TECHNOLOGY INC.). This software allowed to obtain the mass and energy balance, which were needed to estimate the technical, economic and environmental prefeasibility of the process [12]. The chemical characterization and results obtained in the experimental part were the starting point of the simulation.

2.4.1. Stand-alone process

For simulation effects, the amount of raw material considered was 10 T/h. To define the antioxidant extract composition, the two major components of the thyme extract were taken into account in equal fractions, which are reported and correspond to thymol and p-cymene [13][14]. The first part of Figure 1 presents the conventional extraction process. The process begins when the thyme inlet in an oven to be dried at 40°C until reaching moisture of 10%. Then, the solid is grinded to particle size below 400 μm in order to allow a proper extraction condition, this was carried out in a miller.

Subsequently, the reduced size solid is directed to the extraction vessel.

Once the raw material was pretreated, it enters in the extraction vessel, where it comes in contact with the solvent in a 20:1 solvent-solid ratio (%v/w). The extraction was carried out at 40°C with a residence time of 3 hours. After the extraction process, the stream passed through a filter to obtain two streams, one including the exhausted solid and a second one including the hydro-ethanolic antioxidant extract. The antioxidant extract passes through three evaporators to recover the most quantity of ethanol-water. Those evaporators have vacuum conditions.

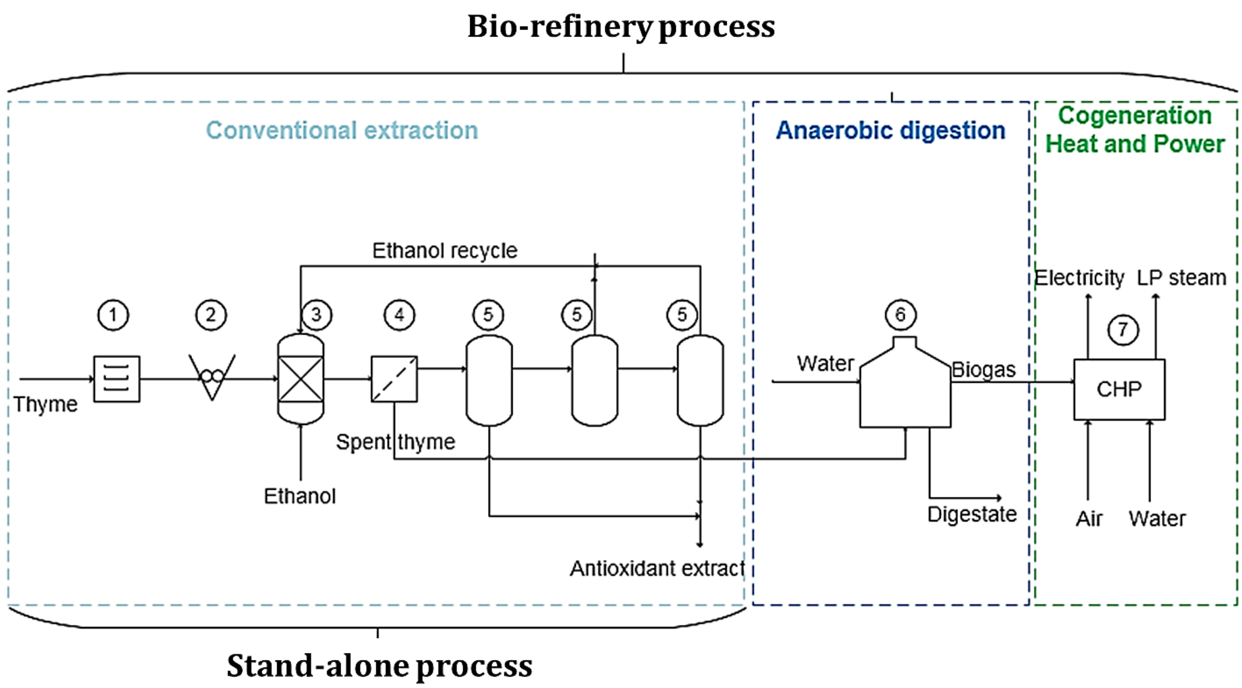

Figure 1. Process flow diagram. 1) Dryer 2) Mill 3) Extraction vessel 4) Filter 5) Evaporator 6) Anaerobic digestor 7) Cogeneration system.

2.4.2. Biorefinery process

The biorefinery process consists of three stages: conventional extraction, anaerobic digestion and cogeneration system, this process is shown in Figure 1. The anaerobic digestion process for the production of biogas was carried out with the thyme remaining of the extraction [15]–[17]. The temperature for the anaerobic reactor was 37°C for anaerobic digestion in mesophilic conditions. The biogas production was simulated considering the experimental yield obtained.

To simulate the cogeneration system, it was considered that only methane offers the calorific power resulting from combustion. In the simulation, the air was compressed to reach 10 bar as was reported by Solarte-Toro *et al.* [18] and the combustion temperature was 1000°C (an average of the combustion temperature) [19]. The combustion gases passes through a turbine where the pressure was decreased until 1 bar and generates work as product. Then, the hot gases passes through a simultaneous heat exchanger to heat up the pressurized water and to produce low pressure steam with 10% temperature excess to avoid condensation.

2.4.3. Economic assessment

The economic analysis was performed using the Aspen Process Economic Analyzer software (ASPEN TECHNOLOGY INC). This software allows to calculate the equipment cost and the energy requirements. To evaluate the economic viability, prices and economic data used in this analysis correspond to Colombian conditions such as the costs of the raw materials, income tax, labor salaries, among others. Additionally, the straight-line method was selected for depreciation and a period of 10 years was chosen. The process was evaluated considering 330 days and 24 h/day of operation, this means 7920 h/year [20].

Due to the whole thyme plant is used, the cost of thyme was considered as the production cost of the crop in the first year [21]. A reference sale price of a hydro-ethanolic extract of thyme was taken [22]. Only a percentage of this price was taking into account due to the concentration of the extract obtained in this work is lower than the reference product. Respect to equipment cost estimation, two extractor vessels was considered with 90 minutes of residence time each one, to simulate a continuous process and the residence time of anaerobic digestor was 15 days. Table 1 show the costs of raw materials, products, utilities and the operation data used for the economic assessment.

Table 1. Data used for the economic assessment

Feature	Value	Unit	Reference
Raw materials			
Thyme	0.65	USD/kg	[21]
Water	2*10-3	USD/kg	[23]
Ethanol	0.45	USD/kg	[24]
Product			
Antioxidant extract of thyme	0.5	USD/kg	[22]
Operation			
Low pressure steam	1.57	USD/T	[25]
Electricity	0.14	USD/kWh	[25]
Fuel	24.58	USD/MW	[25]
Operator labor cost	2.14	USD/h	[25]
Supervisor labor cost	4.29	USD/h	[25]

2.4.4. Environmental analysis

The environmental evaluation of the process was performed using the software WAR GUI (Chemical Process Simulation for Waste Reduction) developed by United States environmental Protection Agency (EPA). The method is based on a potential environmental impact (PEI) balance for chemical processes. The PEI is a relative measure of the potential for a chemical or stream waste to have an adverse effect on human health and the environment [26]. WAR algorithm evaluates the PEI in terms of eight categories: Human Toxicity Potential by Ingestion (HTPI), Human Toxicity Potential by Exposure (HTPE) dermal or inhalation, Terrestrial Toxicity Potential (TTP) Aquatic Toxicity Potential (ATP), Global Warming Potential (GWP), Ozone Depletion Potential (ODP), Photo-Chemical Oxidation Potential (PCOP) and Acidification Potential (AP) [27].

3. Results

3.1. Characterization

The standard methods were used to perform the chemical analysis of the raw material, the results are shown in Table 2.

Table 2. Characterization of thyme (%w/w dry basis).

Component	Percentage [%]
Extractives	31.28 ± 1.19
Cellulose	31.52 ± 2.04
Hemicellulose	17.04 ± 1.96
Lignin	14.87 ± 1.01
Ash	5.29 ± 0.09
Total solids	29.54 ± 1.49
Volatile solids	27.05 ± 0.38
Moisture*	75.29

*Moisture of fresh raw material

In the work reported by Kaloustian et al. (2003) [28], the structural characterization of whole thyme is shown under different conditions of precipitation and climate. Those values are closer to the obtained in the present work. Thyme has a very high percentage of initial moisture, which is common in plants and it is responsible of consistency and nutrient transport in the plant [29]. The water content does not provide energy and can mean a high energy cost as pretreatment due to its high content in the raw materials. Some biomass components are not digestible and are not absorbed, this is the case of lignin [29]. The total solids content allow to know the quantity of mass in the raw material, it is use to describes the dry matter, since avoid the water content. Then, the volatile solids content allow to know the quantity of organic matter [30], this is the matter available for biological treatments. Due to the amount of volatile solids corresponds to approximately 92% of the total solids, it is possible to affirm that the thyme is a raw material with high feasibility of biodegradability.

3.2. Conventional extraction and Biochemical Methane Potential (BMP)

The extraction yield of thyme in this work was 11.95%, this result is comparable with that presented by Hamdy *et al*. [31] which was 14.80%. However, the difference may be due to the extraction performed in the other work was during 72 h, shaking, room temperature and the ratio raw material: solvent was 1:50.

The production yield of biogas from thyme in 15 days was 231 ml/g VS and the yield of methane production was 114 ml/g VS, which represents that the methane content is approximately 50%. The methane yield of methane is comparable with the yield obtained by Martinez *et al.* [32], which was of 113 ml/g VS, in that work residues of phenolic-compounds extraction of grape were used for biogas production.

3.3. Economic assessment

The comparison between a stand-alone and biorefinery process using thyme as raw material was carried out for a base case of 10 T/h of thyme. The utilities requirements for plant operation in the biorefinery approach can be self-sustainable in terms of the cooling water and energy requirements, since the use of biogas in the cogeneration allows to supply the energetic requirement and the cooling water can be used coming from the wastewater treatment. For the steam requirement, cogeneration in the biorefinery approach supplies only 1% of the requirement due to the high requirement in the drying of raw material.

Table 3. Economic assessment results

Process	Scale		Payback period (years)	NPV (mUSD)
Stand-alone	Base case	240 T/day	3.38	7.78
	Minimum scale	80 T/day	10	0
Biorefinery	Base case	240 T/day	5.79	3.92
	Minimum scale	150 T/day	10	0

Table 3 shows the results of economic assessment. In the stand-alone process, the base case is profitable in 3.38 years in the project lifetime with a present value (VPN) of 7.78 mUSD/year. The minimum raw material flow in which the stand alone process can operate, this means, the flow in which neither losses nor profits are generated, is 80 T/day. For the biorefinery process, the base case is profitable in 5.79 years with a present value (VPN) in the project lifetime of 3.92 mUSD/year. The minimum raw material flow in which the biorefinery process can operate is 150 T/day. The results shown allow affirming that both the stand alone and biorefinery process are profitable. For the biorefinery approach takes more time the payback period than in the stand-alone process, this is because for the biorefinery it is necessary to take into account the expense of the equipment for anaerobic digestion and cogeneration, and therefore their operating costs.

3.4. Environmental analysis

Table 4 shows the results obtained from the environmental analysis carried out with the software WAR GUI. It was found that 2 of the eight categories evaluated generate more environmental impact, those are GWP and AP. The biorefinery approach has more impact in comparison with stand-alone process, the last may be due to the carbon dioxide release for the anaerobic digestion and the digestate.

Table 4. Potential Environmental Impact (PEI) leaving the system per mass of product

Category / Process	HTPI	HTPE	TTP	ATP	GWP	ODP	PCOP	AP	Total
Stand-alone	3.77E-10	1.03E-9	3.77E-10	1.31E-7	7.59E-7	2.88E-12	5.55E-10	7.86E-6	8.75E-6
Biorefinery	9.62E-10	3.25E-7	9.62E-10	3.33E-7	5.01E-6	7.34E-12	1.41E-9	2E-5	2.57E-5

Conclusion

The results showed the pre-feasibility of extract antioxidant compounds from thyme as raw material by solvent extraction through stand-alone and biorefinery approach. But with the conditions proposed in this paper, the stand-alone process approach is more viable than the biorefinery approach. However, there are different ways of making the processes more profitable in which the biorefinery could be more profitable than the stand-alone approach. This interest is important due to the fact that the total use of raw materials is essential to avoid contamination and to get more profitability in the process.

Other important aspect assessed in this study case, is the potential environment impact (PEI) as environmental indicators. It was achieved that less PEI in the stand-alone than biorefinery approach. It is important to note that efforts have to be made for valorizing the waste generated in the anaerobic digestion, future studies have to be made in order to validate this possibility.

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