OLIVE POMACE VERSUS NATURAL GAS FOR METHANOL PRODUCTION: A LIFE CYCLE ASSESSMENT

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Abstract:

Increasing demand for methanol production and global competition for the use of natural resources are key issues in finding new and environmentally routes for methanol production. In this work, life cycle assessment was performed using software SimaPro v9 to analyse the environmental impact of methanol production process from olive pomace and compare with natural gas route. The main stages considered in the methanol production from olive pomace were: olive production, olive oil extraction and methanol production. In addition, the methanol production in turn can be divided in three main processes, olive pomace gasification, syngas purification and methanol production which were also evaluated individually. Finally, the global environmental impacts associated with the methanol production from olive pomace was compared with a conventional methanol production from natural gas. This assessment determined that the production of methanol from the olive pomace had a greater environmental impact for all the categories studied except the one related to the shortage of fossil fuels. These results were directly related to the technical performance of the processes.

Keywords: Gasification; olive pomace; natural gas; methanol; LCA; SimaPro v9.

1. Introduction

Nowadays, methanol is one of the highly synthesised chemicals around the globe, being a key molecule in both our daily lives and the global economy (Demirbas 2007). This alcohol can be used directly as a clean fuel or can be mixed with other specific fuels. From a thermodynamic point of view, the use of methanol in internal combustion engines could have many benefits, such as a considerable increase in power and energy efficiency (Amigun et al. 2010). Furthermore, it is essential for the synthesis of other chemical products such as paints, solvents, formaldehyde, gasoline and polymers, among others.

Worldwide, there are currently around 90 industrial plants which have a production capacity of about 110 million ton (Methanex). Each day, nearly 0.2 Mt of methanol are used as a chemical feedstock and transportation fuel. In addition, the global methanol production has increased significantly in recent years due to its widespread use in the chemical and process industries and the development of olefins and fuel cells industries in Europe (Pérez-Fortes et al. 2016). However, European methanol demand is becoming increasingly dependent on imports to feed its market (ICIS).

Conventionally, the methanol is principally produced from fossil fuel, mainly through natural gas reforming with steam. The main problem associated with the methanol production from fossil resources are the emissions of large amounts of greenhouse gases (GHG). Moreover, these emissions of methanol production depend on process configuration and feedstock (in the range from 462 to 2965 kg CO_2 eq/t methanol) (Kajaste et al. 2018).

However, the last climate change study published by the Intergovernmental Panel on Climate Change (IPCC) (IPCC) established that use of fossil fuels must be reduced by half in under 15 years and eliminated completely in 30 years to reduce emissions of greenhouse gases. Thus, due to the environmental policies are increasingly rigorous and moreover, most of these fuels are imported from outside the EU, the interest in researching new sustainable alternatives has increased. Among the non-fossil production alternatives, methanol obtained through biomass gasification is considered as a suitable candidate to replace conventional methanol from natural gas, helping to reduce climate change and diminishing such a dependence.

Olive pomace biomass is a large resource in Mediterranean countries, especially in Spain, since it is the world's leading olive oil producer and exporter, accounting for about half of total global production (Commission 2019). In addition, previous works have demonstrated that olive pomace is a suitable feedstock for methanol production. In this regard, methanol production from syngas obtained through biomass gasification was simulated using Aspen Plus® (Puig-Gamero et al. 2018), being the aim to simulate, validate and optimize, but above all, demonstrate its technical feasibility. However, important economic or environmental aspects were ignored. In a second study, the economic viability of this plant was carried out demonstrating that the methanol production through olive pomace gasification was highly probable would be profitable (Puig-Gamero et al. 2020). Nonetheless, its suitability needs to be confirmed by carrying out economic and techno-environmental analyses upon which decision can be made. Hence, this paper focused on environmental assessment, since this is essential to achieve a sustainable future.

Currently, one of the most used tools for evaluating the environmental impacts associated with a product, process or activity is the Life Cycle Assessment (LCA). LCA is a standardized methodology in accordance with ISO 14040 and 14044 standards (Standardization 2006a; Standardization 2006b). Hence, this analysis involves the complete cycle of the product, process or activity, including the extraction and feedstock processing, production, transportation and allocation, use, recycling and final disposal of the product. In this sense, LCA helps to identify weaknesses and features of the product that could be improved to reduce environmental impacts and use fewer resources in the life cycle stages.

Several studies on the LCA associated with the methanol production have been recently reported. Different authors (Renó et al. (2011) [11], Tangviroon et al. (2014) [12] and Yadav et al. (2020) [13]) studied the LCA of the methanol production from biomass, concretely, sugarcane bagasse, soybean oil and wood, respectively. For its part, Li et al., compared the LCA of methanol production from coke oven gas, coal and natural gas (Li et al. 2018). Gao et al., analysed the coal-to-methanol production and identified that this process produced significant emissions of GHG (Gao et al. 2018). Lerner et al., studied the best conditions to reduce the GHG for methanol production from natural gas (Lerner et al. 2018). Moreover, the comparison of different raw materials (coal, natural gas, flue gas, corn, and wood biomass) was studied by Kajaste et al. (Kajaste et al. 2018).

On the other hand, there are studies focused on LCA associated with olive pomace valorization. In this sense, Parascanu et al., carried out the environmental assessment of olive pomace valorization through pyrolysis, combustion and gasification (Parascanu et al. 2018a; Parascanu et al. 2018b). Duman et al., studied the LCA of olive pomace utilization in Turkey. For that purpose, they analysed different scenarios involving producing fuel pellets, fodder additives and composting (Duman et al. 2020). In addition, Uceda-Rodriguez et al., evaluated the environmental benefits associated with the addition of olive pomace for the manufacture of lightweight aggregates (Uceda-Rodríguez et al. 2020).

However, to the best of the authors’ knowledge, there are not environmental assessment of the olive pomace valorization through gasification for its subsequent use in the production of methanol. Hence, the main aim of this study was to compare in terms of environmental impact, the methanol production from natural gas (conventional methanol production) and from syngas obtained by olive pomace gasification. Additionally, the environmental impact performed for each process involved in methanol production from olive pomace was also evaluated.

2. Methodology

The LCA study was carried out according to the ISO 14040 standard (Standardization 2006b), which recommends four main steps: goal and scope definition, life cycle inventory analysis, environmental impact assessment and interpretation of the results.

2.1 Goal and scope definition

The aim of this study was to compare in terms of environmental impact, the methanol production from natural gas (conventional methanol production) and from syngas obtained by olive pomace gasification. For that purpose, the LCA was carried out using SimaPro v9 software. Besides, it was performed in accordance with the cradle to gate approach, including all the phases involved from raw materials extraction to methanol production. Moreover, the functional unit was defined as 1 kg of methanol.

Figs 1 and 2 show the diagram of the system boundaries for the methanol production from olive pomace and natural gas, respectively. As can be seen, the main stages considered in conventional method were the natural gas extraction, importation and methanol production, while for methanol production from biomass the main stages considered were: olive production, olive oil extraction and methanol synthesis. In addition, the three main processes involved in the methanol production were also studied.

In order to carry out the LCA, several hypotheses have been considered in order to avoid overlapping in the decision-making process:

- Planting and tree growth have been omitted due to the long time in which there is no production.
- The transport of olive to the olive oil mill and the transport of fertilizers have been considered.
- The acquisition and the maintenance of the agriculture machinery are not considered.
- The acquisition and the maintenance of machinery used to extract the natural gas and gas pipeline are not deemed.
- The equipment involved in the methanol plant are excluded from the assessment.
- The olive oil mill and the methanol plant are located at the same place. Thus, the biomass transport in this last case has not been considered.
- Desulfurization process of conventional method for producing methanol was not taken in account.

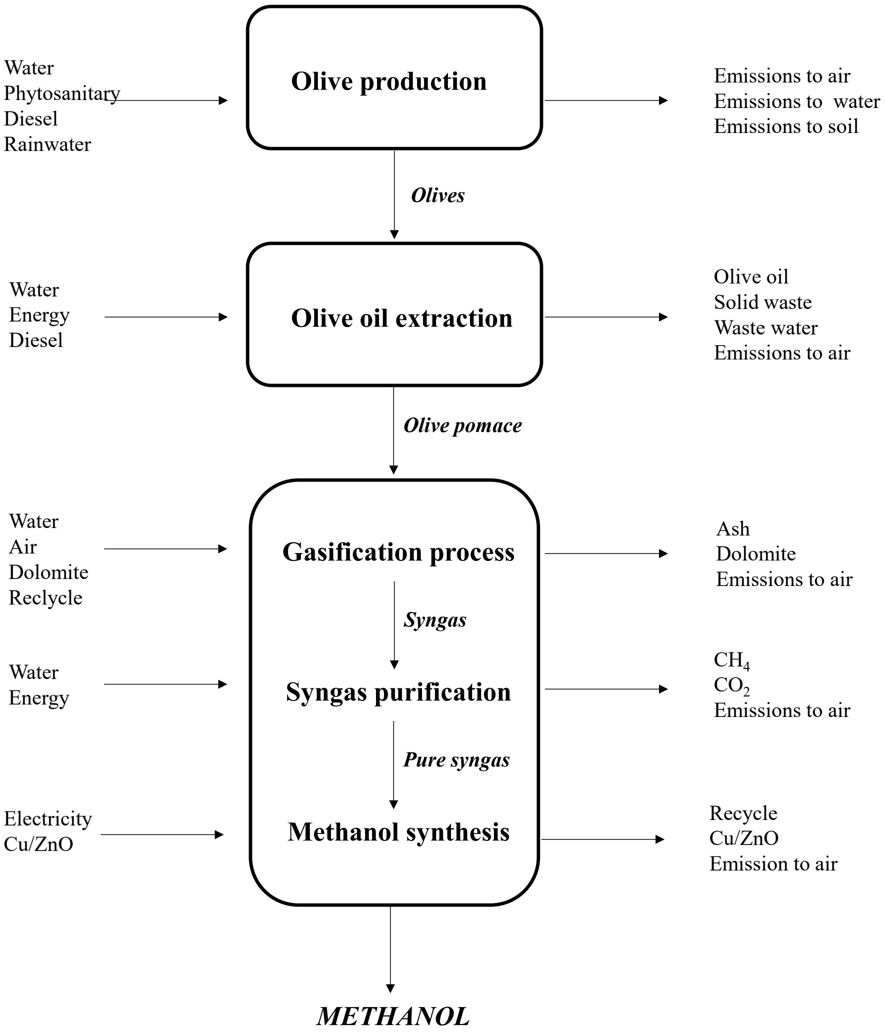

Fig 1. System boundary of methanol production from olive pomace gasification.

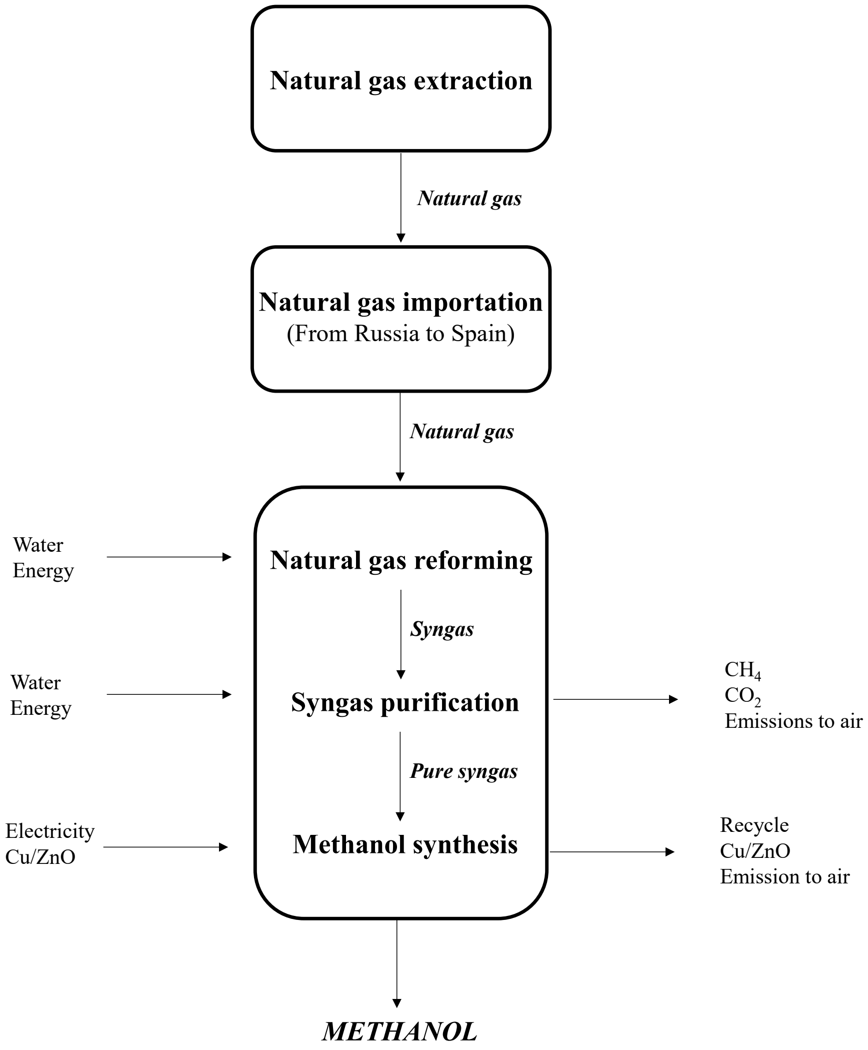

Fig 2. System boundary of methanol production from natural gas.

2.2 Life cycle inventory analysis

2.2.1 Methanol production from olive pomace gasification

The inventory data, such as the direct inputs and outputs of each stage considered in the boundary system, were collected from a real olive mill plant, the Aspen Plus® software and the Ecoinvent database (Ecoinvent, 2017). The olive production and olive extraction stage were explained in detail in previous works (Parascanu et al. 2018a; Parascanu et al. 2018b).

a) Olive production stage

Table 1 summarizes the inventory data used which were provided by the real olive mill plant *Aceites García de la Cruz* located in Toledo (Spain). These data were processed to determine the corresponding values for the functional unit. On the other hand, the air, water and soil emissions associated with the olives production stage were taken from the Ecoinvent 3.4 database (Ecoinvent, 2017). Table 2 shows the main input and output of the agricultural stage referred to functional unit (1 kg of methanol).

b) Olive oil extraction stage

Once the olives were harvested, they were transported to the oil mill to produce the olive oil. In this case, all collected data were obtained from *Aceites García de la Cruz* olive oil mill (Table 3). Table 4 lists the main input and output of the olive oil extraction stage referred to functional unit (1 kg of methanol).

Finally, economical allocation was used for the olive pomace, since the physical allocation is not appropriate due to the byproduct is much higher than the main product and, thus, this assumption can result in important estimation errors. In this sense, to prevent unfairness, the price of the product and by-products has been used to calculate the allocation keys (Parascanu et al. 2018b). In this way, the economic allocation factor for the olive oil was 97.2 % (the average price for 1 kg of extra olive oil is 3.65€ /kg and the average yield is 18.5 %), for the olive pomace was 1.7 % (the average price for olive pomace is 15€ /ton and the average yield is 73.5 %) and for the olive stone was 1.1% (the average price of olive stone is 90€ /ton and the average yield is 8 %) (Parascanu et al. 2018b).

Table 1. Information considered for olive production stage (provided by *Aceites García de la Cruz* olive oil mill).

Final product	Olives
Harvest year	2015/2016
Growing area (ha)	40
Conversion factor (kg olives/ha)	718
Means of transport	Truck
Irrigation system	Rainwater
Rainwater collected (m^3/ha)	2140
Fertilizers transport (km)	285
Phytosanitary treatment (L)	4500, twice a year
Total diesel consumed (L/ha)	24.2

Table 2. Inputs and outputs for the olive production stage, considering to the functional unit, 1 kg of methanol produced from olive pomace gasification.

	Inputs[*]	
Water	m^3	6.53E-05
Fertilizers	kg	7.51E-6
Diesel	kg	7.46E-06
		Outputs[*]
Olives	kg	2.99
Emissions to air[**]		
NH_3	kg	3.95E-03
CO_2	kg	5.22E-06
N_2O	kg	6.89E-09
NO_x	kg	9.09E-12
H_2O	kg	1.20E-14
Emissions to water[**]		
Cr	kg	1.34E-05
Cu	kg	4.19E-06
Pb	kg	1.04E-06
Hg	kg	3.77E-09
Ni	kg	1.15E-06
NO_3	kg	3.02E-02
P	kg	5.09E-05
H_2O	m^3	5.99E-02
Zn	kg	1.05E-05
Emissions to soil[**]		
Cd	kg	1.98E-06
Cr	kg	7.31E-06
Cu	kg	3.50E-06
Dimethoate	kg	8.95E-07
Pb	kg	7.64E-06
Hg	kg	1.61E-09
Ni	kg	2.70E-06
Zn	kg	3.59E-06

[*] Olive mill plant data; [**] Ecoinvent database

Table 3. Information considered for olive oil extraction stage (provided by *Aceites García de la Cruz* olive oil mill).

Final product	Olive oil
Distance between plot and olive oil mill (km)	19
Means of transport	Truck
By-products	Olive pomace, olive stone, solid waste (leaves, dust and stones)
Factor conversion (kg/ha):	
Olive oil	126.5
Olive pomace	534
Olive stone	57.5
Solid waste	9.4
Operating time (h)	2208
Electrical energy consumed (kW)	78
Water consumption (m^3)	887
Total diesel consumed (L/ha)	24.2

c) Methanol production stage (from olive pomace)

The olive pomace was used as a raw material in this stage. Moreover, Aspen Plus® v9.0 was employed to simulate the process of methanol synthesis from biomass which has been evaluated environmentally herein. The design specifications for modelling the process, the optimization and the validation have been published in a previous study (Puig-Gamero et al. 2018). The processes involved in the production of methanol from biomass are: gasification process, syngas cleaning and methanol synthesis. Firstly, the biomass was gasified at 900 ºC in a double chamber gasifier using steam as gasifying agent and a steam/biomass mass ratio of 0.9. Moreover, dolomite was used as the catalyst to decompose the tar produced. Then, the syngas produced was fed to the pressure swing adsorption (PSA) in which the gas is cleaning and adjusting to achieve a H_2/CO ratio close to 2.4-2.5. Finally, the syngas with the correct ratio is fed to methanol synthesis.

The operating conditions for methanol synthesis were 220 ºC and 55 atm. In addition, due to the low conversions obtained in this process, Cu/ZnO was used as catalyst. Finally, to improve the system performance, the waste stream of methanol synthesis was recycled to the combustion chamber. Figs 3, 4 and 5 show the Aspen Plus® flowsheet of gasification process, syngas cleaning and methanol synthesis, respectively. In addition, Tables 5, 6 and 7 summarize the main block used in each process. Finally, Table 8 lists the main input and output of each process involved in the methanol production from olive pomace (referred to FU).

Table 4. Inputs and outputs of the olive oil extraction stage, considering the functional unit of 1 kg of methanol produced from the olive pomace gasification.

	Inputs*	
Olives	kg	2.99E+00
Water	m^3	1.52E-02
Electrical energy	MJ	2.39E+00
Diesel	L	1.52E-01
	Outputs*	
Olive oil	kg	5.34E-01
Olive pomace	kg	2.23E+00
Olive stone	kg	2.08E-01
Waste	kg	3.92E-02
Emissions to air*		
NO_x	kg	1.20E-04
SO_2	kg	1.94E-05
CO	kg	1.70E-03
PM (particulate matter)	kg	6.25E-05

* Olive mill plant data

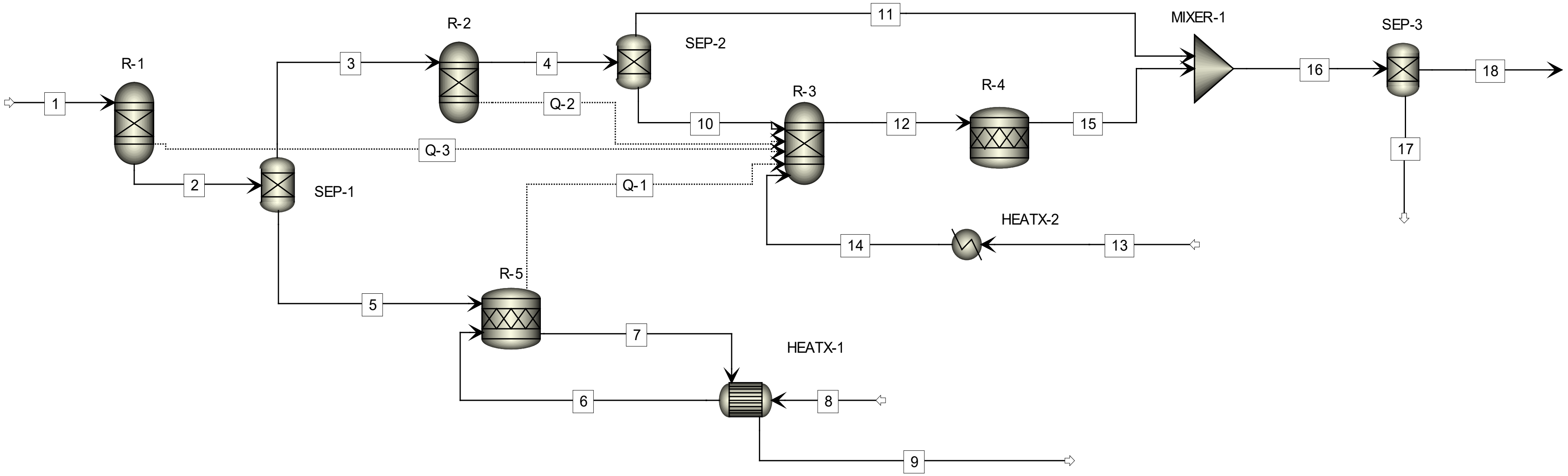

Fig 3. Aspen Plus® flowsheet simulation of the gasification process.

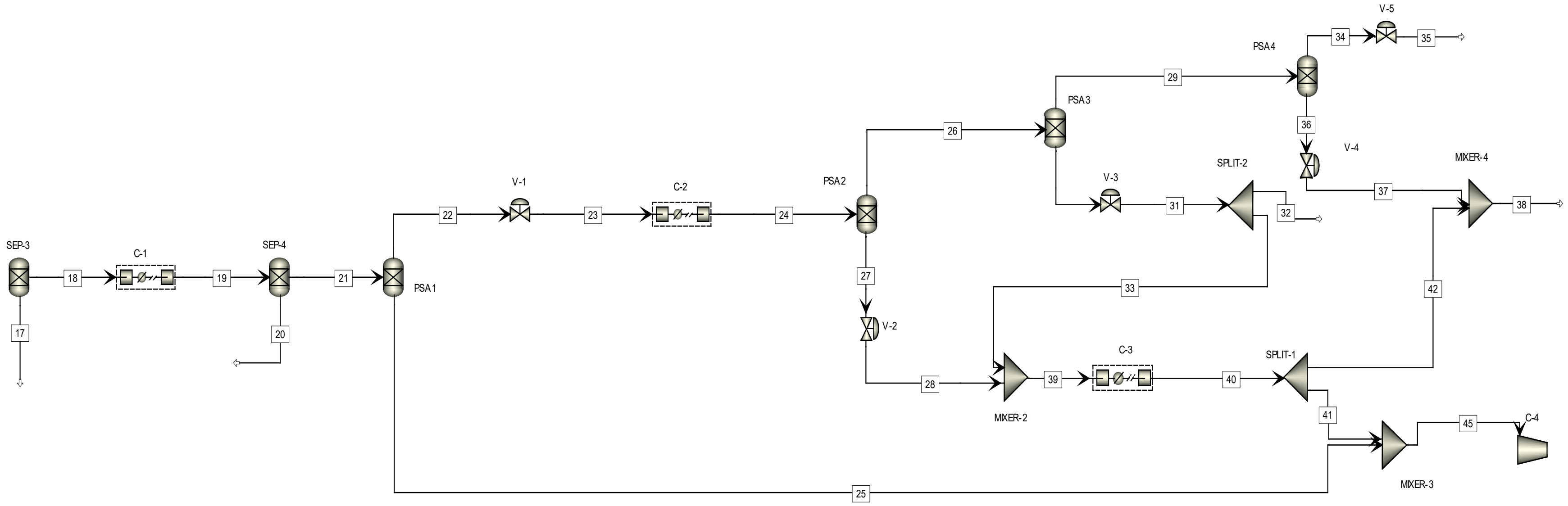

Fig 4. Aspen Plus® flowsheet simulation of the syngas cleaning.

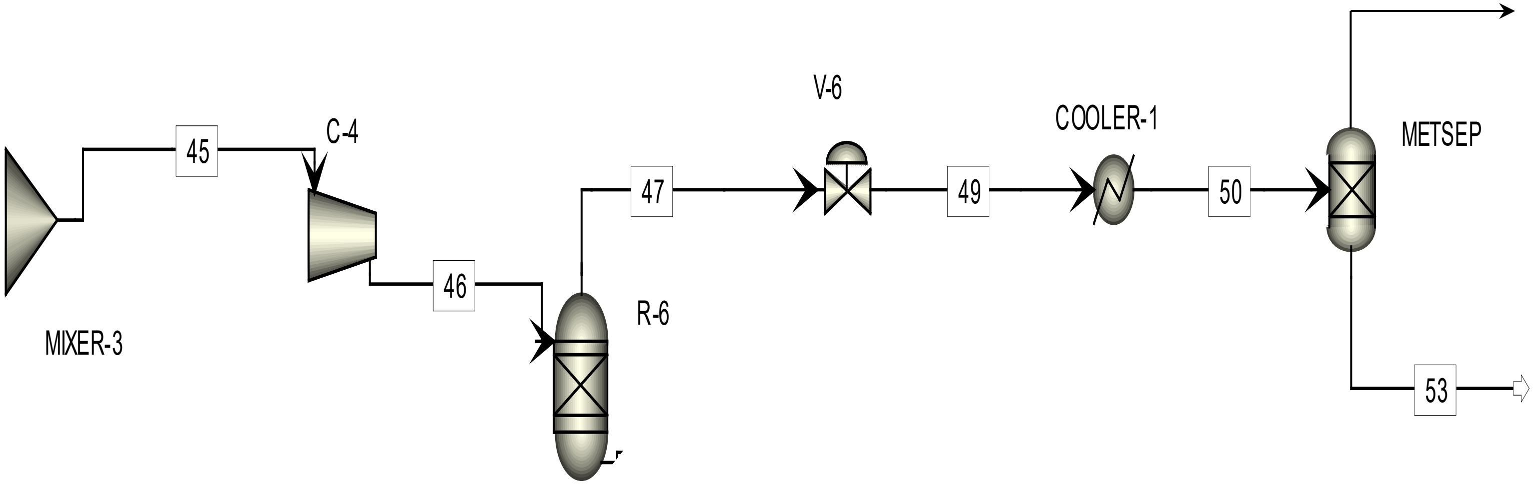

Fig 5. Aspen Plus® flowsheet simulation of methanol synthesis.

Table 5. Blocks description used in the gasification model**.**

NAME	*TYPE*	*DESCRIPTION*
R-1	RYIELD	Biomass pyrolysis reactor, it decomposed the biomass into its compounds and ash. It operated at 1 atm and 900 ºC.
SEP-1	SEP	Separator of the amount of char necessary to achieve the gasification temperature.
R-2	RGIBBS	It models chemical equilibrium minimizing the Gibbs free energy. It was used to produce CO_2, CO, CH_4, H_2S and NH_3. It operated at 1 atm and 900 ºC.
SEP-2	SEP	Separator of H_2S and NH_3 from C, H_2, CO_2, CO and CH_4.
R-3	RGIBBS	Gasifier. It operated at 1 atm and 900 ºC.
R-4	RSTOIC	This reactor allowed to introduce a catalyst. It was used to model the tar reforming using Dolomite as a catalyst. It operated at 1 atm and 900 ºC.
SEP-3	SEP	It separated the active char from the syngas.
R-5	RSTOIC	Char combustion reactor. It operated at 1 atm and 900 ºC.
HEATX-1	HEATX	Exchange heat between the outlet stream from R-5 and the air inlet stream which was warmed up to 150 ºC
HEATX-2	HEATER	Heater to warm up the gasifying agent (water steam) to 150 ºC.

Table 6. Blocks description used in the syngas cleaning model.

NAME	*TYPE*	*DESCRIPTION*
C-1, C-2 and C-3	MULTISTAGE COMPRESSORS	The multistage compressors were used to compress to 30 atm and cool down to 35 ºC the unclean gas, the PSA2 inlet stream and the CO and CO$_2$ mixture, respectively.
SEP-4	SEP	Separator of the water condensed and the syngas.
PSA1, PSA2, PSA3 and PSA4	SEP	Separator to adsorb and separate at 30 and 35 atm rich H$_2$, rich CO, rich CO$_2$ and rich CH$_4$, respectively.

Table 7. Blocks description used in the methanol synthesis.

NAME	*TYPE*	*DESCRIPTION*
C-4	COMPRESSOR	It was used to compress and to purify the syngas.
R-6	REQUIL	Methanol synthesis reactor.
COOLER-1	COOLER	It was used to cool down to 25 ºC the methanol produced to separate it.
METSEP	SEP	Separator of the crude methanol and gas-phase and impurities.

Table 8. Inputs and outputs of the methanol production plant from olive pomace gasification (FU=1kg of methanol) (from software Aspen Plus®).

OLIVE POMACE GASIFICATION		
Inputs		
Olive pomace	kg	2.23E+00
Air	kg	3.28E+00
Water	kg	2.01E+00
Recycling gas*	kg	8.89E-01
Dolomite	kg	2.03E+00
Outputs		
Syngas	kg	3.99E+00
Ash	kg	1.69E-01
Dolomite (waste)	kg	2.03E+00
Emissions to air		
Heat	MJ	2.23E-04
O_2	kg	1.91E-01
CO_2	kg	1.34E+00
H_2O	kg	9.97E-01
N_2	kg	1.71E+00
SYNGAS CLEANING		
Inputs		
Syngas	kg	3.99E+00
Energy	MJ	1.90E+01
Outputs		
Clean syngas	kg	1.93E+00
CH_4	kg	6.29E-02
CO_2	kg	3.14E-01
Emissions to air		
H_2O	kg	9.77E-01
Heat	MJ	2.93E+01
CO	kg	4.91E-01
CO_2	kg	1.71E-01
CH_4	kg	1.01E-03
H_2S	kg	6.03E-03
NH_3	kg	4.00E-02

Table 8. Continuation.

METHANOL SYNTHESIS		
Inputs		
Clean syngas	kg	1.93E+00
Energy	MJ	3.57E-01
Cu/Zn	kg	1.75E+00
Outputs		
CH_3OH	kg	1.00E+00
Recycling gas	kg	9.22E-01
Cu/Zn (waste)	kg	1.75E+00
Emissions to air		
H_2O	kg	4.81E-03
Heat	MJ	4.39E+00

*Waste stream of methanol synthesis was recirculated to gasification process.

2.2.2 Methanol production from natural gas

As above mentioned, the stages involved in the methanol production from natural gas are natural gas extraction, importation and methanol production (Fig 2). The inventory data of the two first stages were collected directly from Ecoinvent database (Ecoinvent, 2017), while the last stage was obtained from the Aspen Plus® software.

a) Natural gas extraction

In this work, importation of natural gas from Russian to Spain was considered since Spanish natural gas reserves are negligible, while Russian is one of the main suppliers to the European natural gas market (Mikulska 2020).

Natural gas production, according to data collected from the Ecoinvent database (reference), occurs through a series of stages: exploration, production, processing and underground storage of natural gas. Gas production ends when gas is fed into the transport pipeline to the country where it will be consumed. This process includes leaks produced during production and the processing of crude oil. The water produced was considered to be discharged into surface waters.

b) Importation of natural gas

The inventory data of natural gas importation stage was also obtained from Ecoinvent database (Ecoinvent, 2017). These data describe the transport to export the natural gas from Russia to Spain in gas pipeline, including in this transport the losses and gas emissions during seasonal storage. The estimated average distance was 7000 km.

c) Methanol production stage (from natural gas)

A methanol production plant from natural gas was simulated using Aspen Plus® to obtain the inventory data of this stage. In the same way than methanol production from olive pomace, this stage can be divided in three main processes: natural gas reforming, syngas cleaning and methanol synthesis. In order to simplify the explanation of the simulation, the three main parts will be explained step by step. The fluid dynamic package selected was Peng-Robinson with Boston Mathias function, being the appropriate for high temperature processes (Pala et al. 2017).

- Natural gas reforming

Fig 6 shows the Aspen Plus® flowsheet of natural gas reforming process. In this work, an equilibrium model based on a Gibbs free energy minimization was used to model a steam reforming reactor. Firstly, the natural gas and steam was comprised at 30 bar and fed to block R-1. In this process, the natural gas reacted with steam at 900 ºC, moreover, in this reactor CH_4, CO_2, CO, H_2O and H_2 were fixed as the main reaction products. Then, the outlet syngas was introduced to PSA system. Table 9 summarizes the main blocks used in steam reforming process.

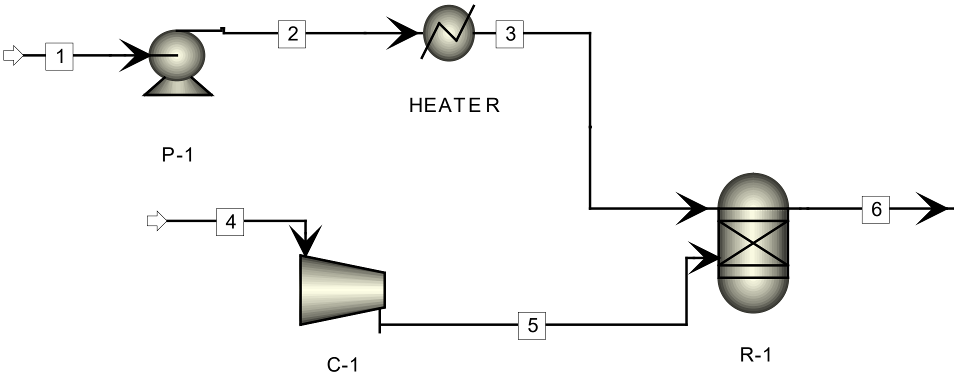

Fig 6. Aspen Plus$^{®}$ flowsheet simulation of the natural gas reforming.

Table 9. Blocks description used in the gasification model**.**

NAME	*TYPE*	*DESCRIPTION*
P-1	PUMP	It was used to compress to 30 atm the water.
HEATER	HEATER	Heater to warm up the water to 280 ºC.
C-1	COMPRESSOR	It was used to compress to 30 atm the natural gas.
R-1	RGIBBS	It was used to model the natural gas reforming and operated at 30 atm and 900 ºC.

- Syngas cleaning: Pressure swing adsorption (PSA)

The aim of this part was to clean the outlet gas of steam reforming to obtain a high-quality syngas which will be used for the methanol synthesis. The outlet gas (stream 6) was introduced into the PSA system, which consisted for four units, as shown in Fig 7. All of them were simulated in a simplified way, by ideal separator, but working at realistic temperature and pressure (35 ºC and 30 atm, respectively) (Gutiérrez Ortiz et al. 2013). Moreover, the percentage of component recovered in the PSA system was obtained from the literature (Gutiérrez Ortiz et al. 2013). Table 10 summarizes the main blocks used in this stage.

Table 10. Blocks description used in the syngas cleaning model**.**

NAME	*TYPE*	*DESCRIPTION*
C-2 and C-3	MULTISTAGE COMPRESSORS	The multistage compressors were used to compress to 30 atm and cool down to 35 ºC the PSA2 inlet stream and the CO and H_2 mixture, respectively.
SEP-4	SEP	Separator of the water condensed and the syngas.
PSA1, PSA2, PSA3 and PSA4	SEP	Separator to adsorb and separate at 30 ºC and 35 atm rich H_2, rich CO, rich CO_2 and rich CH_4, respectively.

- Methanol synthesis

Finally, the syngas was introduced to methanol synthesis reactor. The blocks used to simulate the methanol synthesis are summarized in Table 11 and Fig 8 shows the methanol synthesis flowsheet. In this work, the pressure and temperature of methanol synthesis were 220 ºC and 55 atm.

The syngas was introduced in the R-2 to accomplish the methanol production. The catalyst selected to the synthesis was Cu/ZnO, achieving conversions of 35 % and 17 % for CO and CO_2, respectively (Trop et al. 2014). Then, reaction product was depressurized to 1 atm and cooled down to 25 ºC to condense and separate the crude methanol form the gas-phase in the METSEP flash. Finally, stream 28, which contained unconverted H_2, was compressed and recycled to methanol reactor again. Finally, Table 12 lists the main input and output of each process involved in the methanol production from olive pomace (referred to FU).

Table 11. Blocks description used in methanol synthesis.

NAME	*TYPE*	*DESCRIPTION*
C-4	COMPRESSOR	It was used to compress and to purify the syngas.
R-6	REQUIL	Methanol synthesis reactor.
COOLER-1	COOLER	It was used to cool down to 25 ºC the methanol produced to separate it.
METSEP	SEP	Separator of the crude methanol and gas-phase and impurities.

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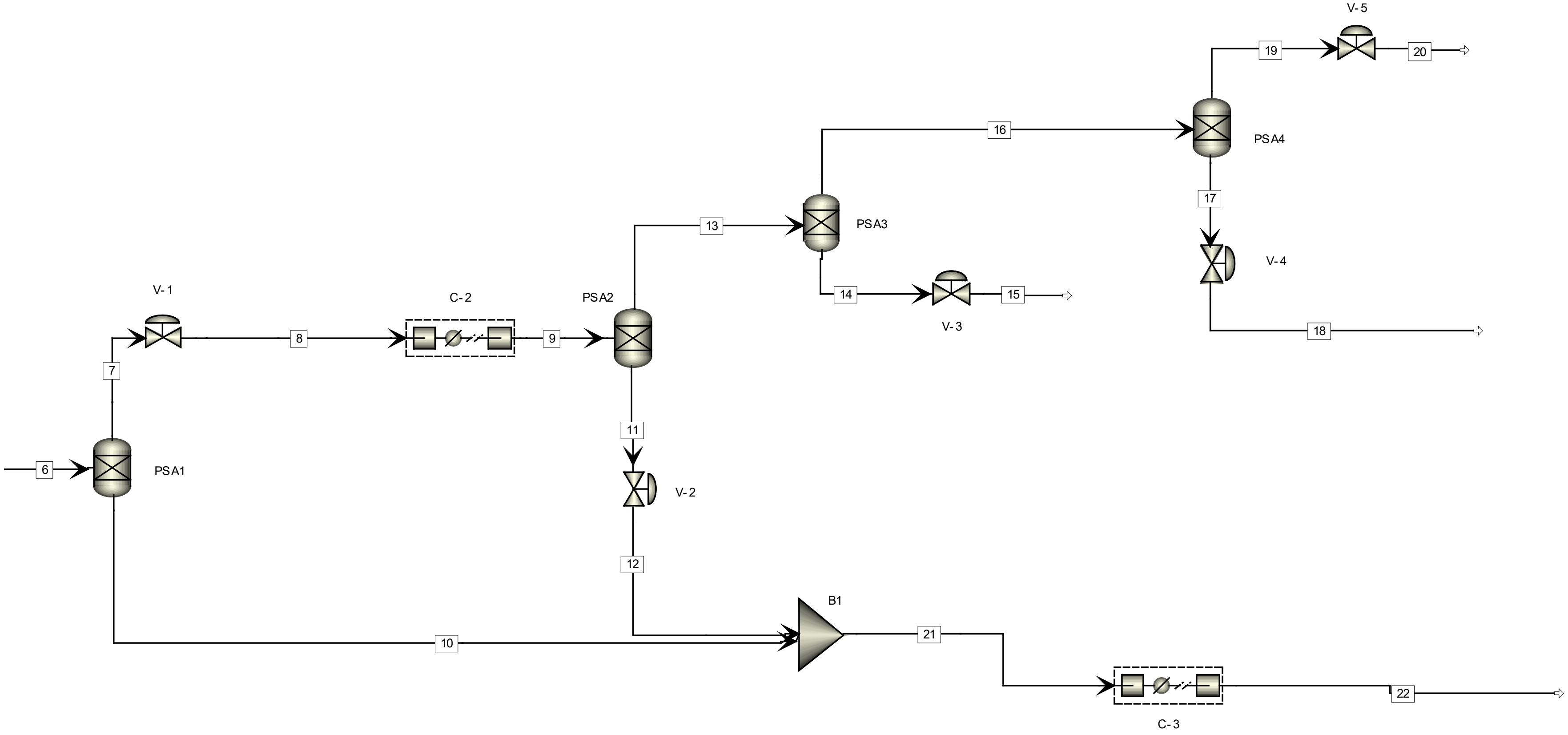

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361 **Fig 7.** Aspen Plus® flowsheet simulation of the syngas cleaning.

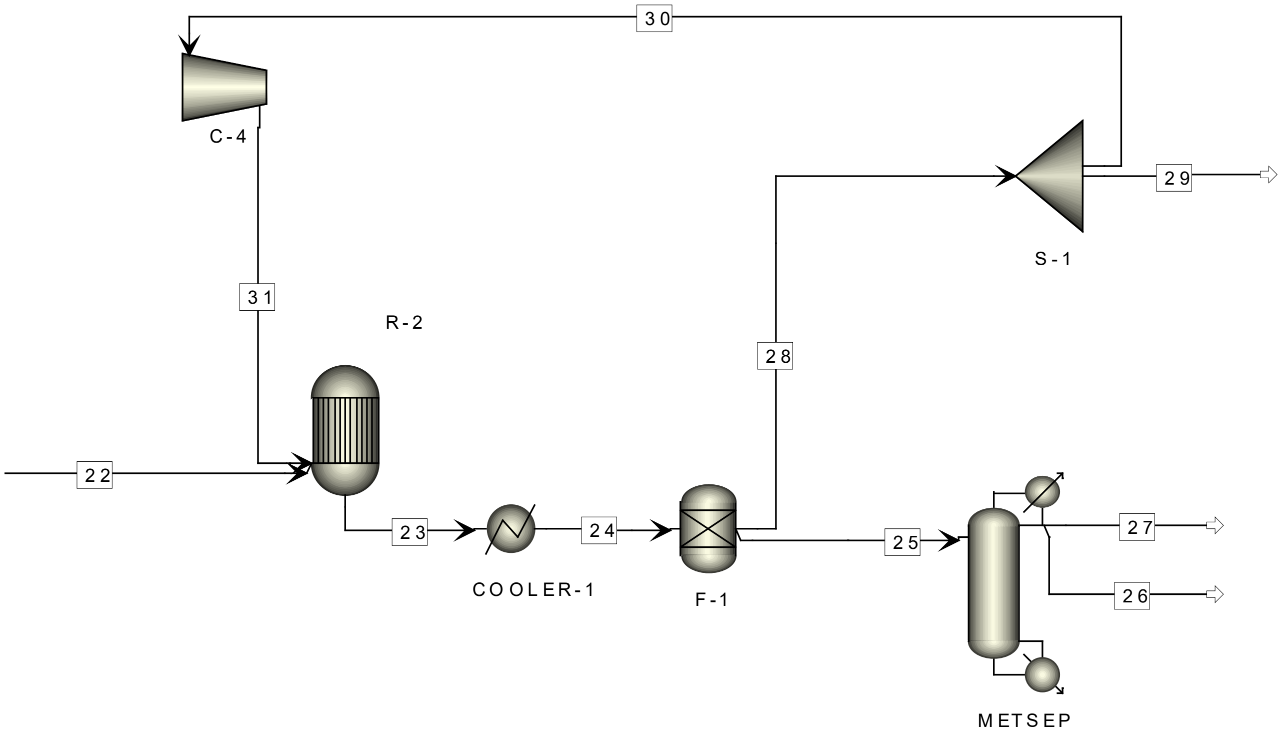

Fig 8. Aspen Plus® flowsheet simulation of methanol synthesis.

Table 12. Inputs and outputs of the methanol production plant from natural gas (FU= 1kg of methanol) (from software Aspen Plus®).

NATURAL GAS REFORMING		
Inputs		
Natural gas	m^3	1.17E+00
Water	kg	1.05E+00
Energy	MJ	1.78E+01
Outputs		
Syngas	kg	1.98E+00
SYNGAS CLEANING		
Inputs		
Syngas	kg	1.98E+00
Energy	MJ	7.50E+00
Outputs		
Clean syngas	kg	1.22E+00
CH_4	kg	1.81E-01
CO_2	kg	5.10E-01
Emissions to air		
Heat	MJ	1.36E+01
CO	kg	1.85E-02
CO_2	kg	5.46E-02
METHANOL SYNTHESIS		
Inputs		
Clean syngas	kg	1.22E+00
Energy	MJ	7.62E+00
Outputs		
CH_3OH	kg	1.00E+00
Emissions to air		
Heat	MJ	1.55E+01
CO	kg	3.86E-02
CO_2	kg	1.11E-03
CH_4	kg	2.01E-03
H_2	kg	1.76E-01

2.3 Impact assessment methodology

In this study, the LCA was performed using the software SimaPro v9, which follows the recommendations of the ISO14040 series (Standardization 2006a; Standardization 2006b). Moreover, the methodology used in this research was the Mid-point ReCiPe 2016 due to the fact that the midpoint results have less statistical uncertainty than the endpoint results (Goedkoop et al. 2008). In this sense, the results for the environmental performance associated with the methanol production process from natural gas and olive pomace were calculated for eleven midpoint indicators: global warming potential (GWP); ozone depletion potential (ODP); photochemical oxidation formation potential - humans (HOFP); photochemical oxidation formation potential - ecosystems (EOFP); terrestrial acidification potential (TAP); freshwater eutrophication potential (FEP); marine eutrophication potential (MEP); human toxicity potential - cancer (HTPc); human toxicity potential - non-cancer (HTPnc), fossil fuel potential (FFP), water consumption potential (WCP).

3. Results and discussion

This section presents and discusses the main results obtained from the LCA. Therefore, subsection 3.1 focuses on environmental assessment of methanol production from olive pomace gasification and subsection 3.2 compares the global environmental impacts associated with the methanol production from olive pomace and from natural gas.

3.1 Environmental assessment of the methanol production from olive pomace valorization

Fig 9 shows the assessed environmental performance of the methanol production from olive pomace valorization, considering all the evaluated stages (olives production, olive oil extraction and methanol production) at the mid-point level.

The results obtained showed that the methanol production exhibited the highest impact for the most of impact categories (except MEP and WCP), followed by olive oil extraction. According to Li et al., and Ai et al., (Ai et al. 2006; Li et al. 2018) who studied the LCA of methanol production from different routes, this fact can be attributed to the high energy consumption and greenhouse emissions of the methanol production which are responsible for the impact values of almost all the selected categories. At this respect, the higher GHG emission (CH_4 and CO_2) observed for the methanol production in comparison with olive production and olive oil extraction stages (Tables 2, 4 and 8) could explain the higher GWP, HOFP and ODP impacts of the first one (Fig 9). Although N_2O was emitted in olive production stage, which is about 300 times worse than CO_2 in terms of the greenhouse effect, its existence in traces contributed to a small GWP in comparison with the larger CO_2 emissions. In addition, the methanol production also presented the highest value in the HTPc and HTPnc categories, which includes all the direct toxic effects of human emissions (Parascanu et al. 2018b). This fact can be related to the ash generated and the emissions released into the air (Table 2). Moreover, the inorganic air pollutants, fertilizers and heavy metals (Cd, Pb, Hg, Zn) linked to the first stage can also cause toxic effects (Brentrup et al. 2004). The high NH_3 emissions of methanol production (Oreggioni et al. 2017) directly affected the impact category of TAP. On the other hand, the FFP impact category was directly associated with the diesel and energy consumption (Tables 2, 4 and 8) and indirectly with the demand for natural gas, crude oil or coal required for the background processes (Parascanu et al. 2018b).

A difference trend was observed in the case of the MEP and WCP categories. In this case, the olive oil extraction and olive growing were more affected, mainly due to high values of wastewater generated (Tables 2 and 4) and the large amount of water required for olive production and olives washing in the olive oil mill for olive oil extraction in comparison to methanol production. In addition, the emissions of nitrogen and sulphur compounds (NH_3, NO_x, NO_3 and SO_2) during olive production stage (Table 2) were indirectly responsible for the MEP impact (Goedkoop et al. 2009).

On the other hand, as aforementioned, the methanol production from olive pomace can be divided in three main processes, gasification process, syngas purification and methanol synthesis which were also evaluated environmentally. Fig 10 shows the impact values at the mid-point level using the ReCiPe methodology for each process involved in the methanol production from olive pomace. Syngas purification process was major contributor in most of impact categories assesses since in this stage is where the most of GHG obtained in the gasification process were released into the atmosphere and moreover, the required energy was considerably higher. While the gasification process is autothermal and, therefore, no energy input is required, the purification of the syngas was carried out by means of pressure cycles, and due to the high number of adsorbers, requires large amounts of energy that, compared to the energy required for methanol synthesis, the last one can be considered negligible.

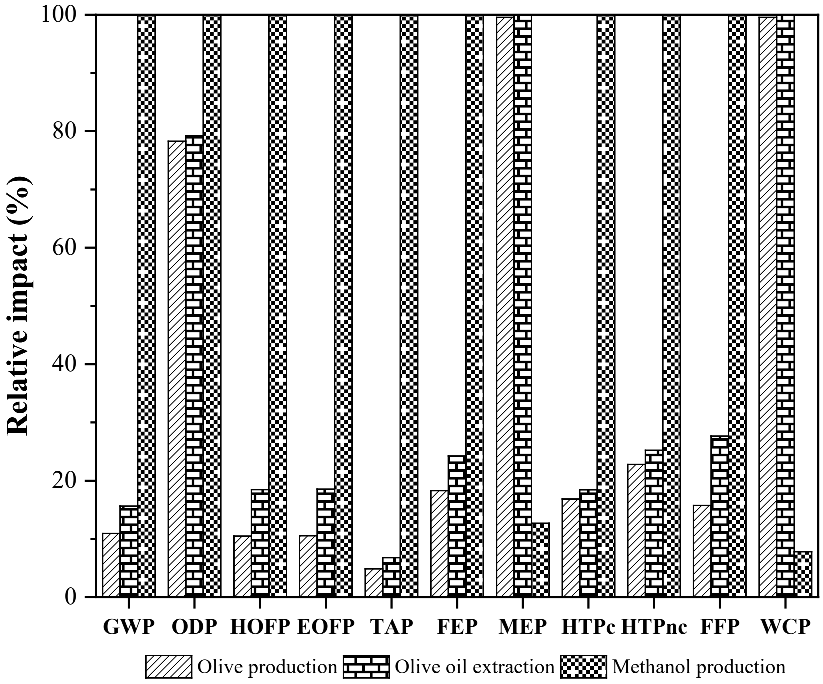

Fig 9. Comparison of the environmental impacts of olive production, olive oil extraction and methanol production stages.

As commented before, the GWP, ODP and HOFP categories were directly influenced for the CO_2 and CH_4 emissions. Syngas purification showed the highest value for GWP and HOFP followed by gasification. In the case of gasification process, GWP impact was associated with combustion chamber where a high amount of CO_2 was released due to char combustion. While, the methanol synthesis had the least influence on GWP category due to the waste stream were recycled, thus, the impact could be associated with the background processes to obtain the required energy. However, this last process showed the highest impact value for ODP, which could be associated with the higher heat emissions of this stage (Table 8). Concerning MEP and WCP categories, the high value obtained by gasification and purification process can also be attributed to the high water consumption as agent gasifying and as refrigerant, respectively. Finally, the HTPc and HTPnc categories presented similar values for three process, being associated with the emissions to air.

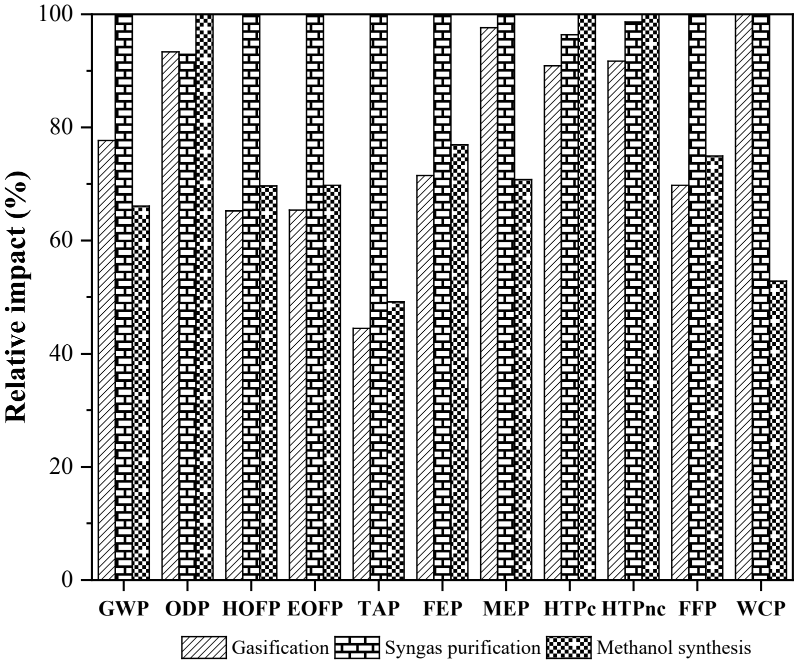

Fig 10. Comparison of the environmental impacts of three processes involved in the methanol production from olive pomace.

3.2 Comparison between methanol production from olive pomace and natural gas

Finally, the comparison between methanol production from olive pomace and natural gas, considering all stages was carried out, since it was the main aim of this work. In this sense, Fig 11 displays for the two routes of methanol production the impact values at the mid-point level using the ReCiPe methodology. Table 13 shows the aggregated according to ReCiPe Mid-point methodology for each methanol production route. As can be observed the olive pomace route presented at the mid-point level higher values for all the impact categories than the natural gas one. The reason that olive pomace route leads to higher environmental contribution was probably due to the low methanol efficiency (0.4 kg methanol and 1.2 kg methanol per kg of olive pomace and natural gas, respectively) and thus, high CO_2 emissions are produced per kg of methanol (FU) during olive pomace route. But, it is also due to the environmental impacts of the previous stages (olive production and olive oil extraction in comparison to extraction and importation of natural gas). It was identified that methanol yield of natural gas route was three times greater than olive pomace route. Therefore, the latter route presented outstanding disadvantage when the data was normalized considering the FU. Moreover, it should be noted that the desulfurization process for natural gas route, which can be associated with large amount of required energy, was not taken in account.

Regarding Table 13, both routes followed the same order of impact magnitude:

- Olive pomace to methanol: GWP > FFP > HTPnc > WCP > TAP > HTPc > HOFP = EOFP > FEP > MEP > ODP

- Natural gas to methanol: GWP > FFP > HTPnc > WCP > TAP > HTPc = HOFP = EOFP > FEP > MEP > ODP

The GWP category had the highest value compared to the other impact categories for both routes which was caused mainly by GHG emissions, the energy consumption and heat releases (Tables 2, 4, 8 and 11). In the case of FFP category which was lower for olive pomace route was mostly affected by the energy necessary to carry out the processes (background system). Moreover, the extraction of natural gas was the main contributor to this category for methanol production from natural gas route. The HTPc and HTPnc was higher for the olive pomace route which can be related to the ash generated and the emissions released into the air (Table 2), but also fertilizers and heavy metals (Cd, Pb, Hg, Zn) related to olive production. For both routes, the HTPc presented lower values than HTPnc category.

Furthermore, it can be seen in Fig 11 that WCP and MEP categories was insignificant in the methanol route, which was directly associated with the high amount of water consumed in olive pomace production and olive oil extraction. The high nitrogen and sulphur compound emissions of methanol production in olive pomace route (Oreggioni et al. 2017) directly affected the impact category of TAP.

Finally, the FEP, MEP and ODP were associated with the emissions that are produced during the energy production in the background system and the releases of nitrogen and sulphur compounds, being higher in the case of olive pomace route.

According to the results, methanol yield from olive pomace is disadvantaged due to its lower H_2 content in comparison with natural gas. In this regard, the co-gasification of olive pomace with other types of feedstock could produce synergistic effects during the process, thereby further improving gas yield and quality. Thus, it could be a good alternative to enhance the gasification process and, thus, the methanol yield, leading to environmental improvements.

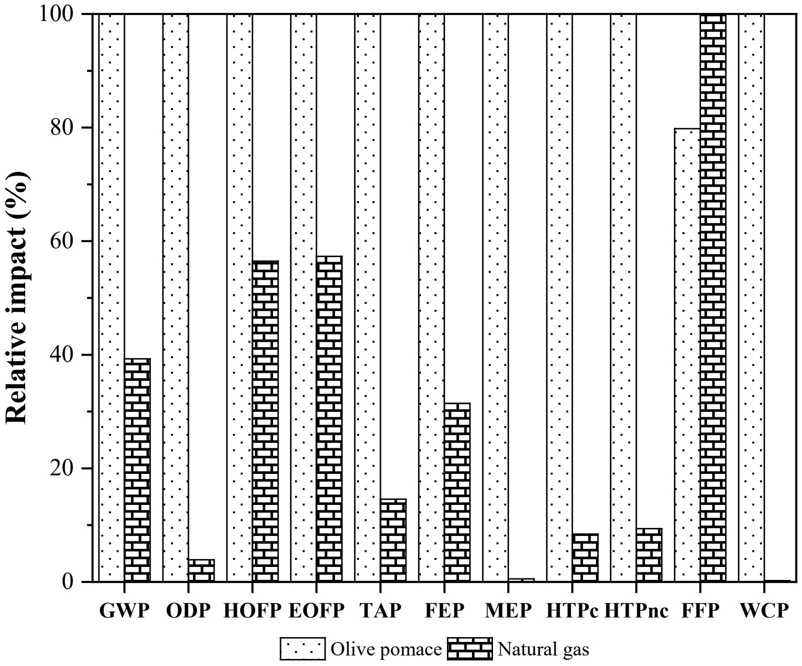

Fig 11. Environmental impact for methanol production form olive pomace and natural gas, associated with the functional unit 1kg of methanol (ReCiPe mid-point).

Table 13. Impact assessment results of methanol production routes referred to FU considering the cradle-gate approach.

Impact	Unit	Olive pomace to methanol	Natural gas to methanol
GWP	kg CO2 eq	19.50	8.74
ODP	kg CFC11 eq	6.82E-05	5.74E-06
HOFP	kg NOx eq	0.03	0.02
EOFP	kg Nox eq	0.03	0.02
TAP	kg SO2 eq	0.30	0.05
FEP	kg P eq	5.46E-04	2.44E-04
MEP	kg 1,4-DCB	2.63E-04	2.31E-05
HTPc	kg 1,4-DCB	0.13	0.02
HTPnc	kg 1,4-DCB	1.07	0.15
FFP	kg oil eq	3.21	4.03
WCP	m^3	1.05	0.06

4. Conclusions

In this study a comparison between the methanol production from olive pomace gasification and natural gas was carried out in terms of environmental impact. The results of the analysis showed that, in the valorization of olive pomace, the stage of methanol production had the most significant impact in almost all the categories studied, which was associated with the higher energy required and greenhouse gas emissions produced from last stage. Moreover, the environmental burdens of the main processes involved in the methanol production from olive pomace; biomass gasification, syngas purification and methanol synthesis were also individually evaluated. The results revealed that the greatest environmental impact was obtained by syngas cleaning stage, since the most of GHG releases were emitted in this process and, thus, the required energy was also higher.

Finally, the global environmental effect of both methanol production processes was compared. The results of this comparison determined that the production of methanol from the olive pomace had a greater environmental impact for all the categories studied except the one related to the shortage of fossil fuels. This fact was directly related to the technical performance of the processes and the functional unit deemed. Thus, due to methanol yield from olive pomace route was disadvantaged mainly by differences in composition, the co-gasification of olive pomace with others raw materials could be a good alternative to improve the methanol yield and compete with natural gas.

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Data availability

All data generated and analysed during this study are included in this published article.

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Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

Not applicable

Authors Contributions

María Puig-Gamero: Conceptualization, Data curation, Formal analysis, Investigation, Writing. **María Magdalena Parascanu:** Conceptualization, Data curation, Formal analysis, Investigation. **Luz Sanchez- Silva:** Conceptualization, Funding acquisition, Investigation, Project administration**. Paula Sánchez:** Conceptualization, Formal analysis, Funding acquisition, Project administration.

Competing interests

The authors declare that there is no conflict of interest.