Definition of the desired output from the synthetic process: diesel/SNG ratio

Definition of the desired diesel/SNG ratio

Date: **.../é /2013**

Report Number: **WP4-1-12-01**
Version Number: Final version

Deliverable Number: **D.4.1**
Due Date for Deliverable: 03/31/2013
Actual Submission date: é /.../13
Task Leader: **Kungliga Tekniska Högskolan**

FFW is co-funded by the European Community

Seventh Framework Programme for European Research and Technological Development (2012-2015)

FFW addresses ñ Liquid and gas Fischer-Tropsch

fuel production from olive industry waste: fuel from wasteò

Start date: October 1st 2012, duration: 3 Years

Document Dissemination Level PU

PU = **Public**	
PP = **Restricted to other programme participants (including the Commission Services).**	CL restricted = **Classified with the mention of the classification level restricted "Restraint UE"**
RE = **Restricted to a group specified by the consortium (including the Commission Services).**	CL confidential = **Classified with the mention of the classification level confidential "Confidential UE"**
CO = **Confidential, only for members of the consortium (including the Commission Services).**	CL secret = **Classified with the mention of the classification level secret "Secret UE"**

Document Information

Title	Definition of the desired diesel/SNG ratio
Lead Author	Kungliga Tekniska Högskolan
Contributors	Consiglio Nazionale delle Ricerche
Distribution	Consortium partners. EC
Report Number	D.4.1

Document History

Date	Version	Prepared by	Organization	Approved by	Notes

Acknowledgement

The work described in this publication was supported by the European Communityõs Seventh Framework Programme through the grant to the budget of the FFW project, Grant Agreement Number 308.733.

Disclaimer

This document reflects only the authorsô views and not those of the European Community. This work may rely on data from sources external to the members of the FFW project Consortium. Members of the Consortium do not accept liability for loss or damage suffered by any third party as a result of errors or inaccuracies in such data. The information in this document is provided ñas isò and no guarantee or warranty is given that the information is fit for any particular purpose. The user thereof uses the information at its sole risk and neither the European Community nor any member of the FFW Consortium is liable for any use that may be made of the information.

Summary

The synthetic process implies two separate processes: Fischer-Tropsch synthesis, which leads to the production of diesel, and methanation, which produces synthetic natural gas. The most appropriate ratio between the two fuels will be defined here based on the requirements from the olive industry and the economic advantage which could be obtained taking into account the properties of the catalysts.

The aim of this deliverable D.4.1 *Definition of the desired output from the synthetic process: diesel/SNG ratio* is to define the production ratio between these two fuels which will allow the design of the complete synthetic step. This ratio will affect the Fischer-Tropsch and methanation production processes.

In this deliverable, the energy requirements of the olive oil production process are presented. This information has been used to define the diesel and natural gas amounts required for the production of olive oil, and thus, the required diesel/SNG ratio for this production process.

However, the desired diesel/SNG ratio can differ considerably from that required for the olive oil production process if the amount of biomass produced by olive cultivations is significantly smaller or larger than that to meet the olive oil production energy demands. Therefore, a carbon balance of the whole BTL/BTG (biomass-to-liquid and biomass-to-gas) production process is also presented in this deliverable.

The output of this study shows that the amount of biomass produced from olive cultivations can provide more fuels than these required for the olive oil production process. Finally, a diesel/SNG production ratio is suggested having also in consideration the properties of the FT and methanation catalysts.

Contents

Tables

Figures

1 Introduction

The following document is the deliverable D.4.1 *Definition of the desired output from the synthetic process: diesel/SNG ratio*. The paper is a summary of Task 4.1. *Definition of the desired diesel/SNG ratio* is a part of Work Package 4 ï *Development of technical solutions for SNG-diesel production*.

The objective of WP4 is to develop novel catalysts for FT synthesis which will enhance the overall performance of the process. In the performance of the FT-catalyst both the SNG-production and the Diesel production will be considered. Innovative technology will be applied to the synthesis process for which the catalyst will be optimized taking into account the structure of its support the optimization of its composition and active sites distribution. Apart from this, an economical, industrial medium will be developed for large-scale production of the catalyst.

2 Fuel and energy requirements in the olive oil industry

2.1 Fuel and energy requirements in the production of olive oil

The definition of diesel and electricity requirements in the olive oil production has been estimated from one literature study: a Life Cycle Analysis used to evaluate the consumption of raw materials from olive oil production in Lythrodontas region in Cyprus.

The following table indicates the olive oil production processes in which fuel and energy consumption is required:

Table 1: Specification of processes which require fuel and/or energy consumption in olive oil production (adapted from [1])

Process	Process characteristics considered in the system
Planting the olive trees	Transportation by pickup van, water use
Soil Management	Operation of chisel plough attached to agricultural tractor
Field water supply and irrigation	Operation of electricity generators, electric turbine pumps and sprinkler systems
Fertilizer production and transportation	Production of fertilizers, and transportation by freight ship, lorry and pickup van
Pruning and residue management	Operation on hand-held petrol chainsaw and burning of pruning residues
Pest control	Application of pesticides, operation of compressed air sprayers
Pesticide production and transportation	Production and transportation by freight ship, lorry and pickup van
Collection of olives	Operation of hand-held pneumatic combs
Transportation of olives to processing plant	Transportation by pickup van
Supply of electricity to processing plant	Electricity generation in oil-fuelled power stations

Water supply for processing unit	Operation of pump stations
Water treatment	Operation of plant, production and transportation of treatment chemicals
Olive purification	Operation of conveyor belt, washing machine and electronic scale
Olive grinding and malaxing	Operation of conveyor belt, grinder and mixing vat, water heating
Olive oil extraction	Operation of decanter, separator and pumps, disposal of liquid waste into evaporation pond, part-utilization of pomace as fuel for boiler furnace

In regards to energy consumption of the system described in Table 1, the agricultural and processing stages consume a total of 2.58 kWh of electricity per liter of olive oil produced which is generated by diesel on-site generators. In what concerns fuel consumption, diesel, which feeds agricultural tractors, amounts to 127g, and petrol, which is consumed for operation of chainsaws, amounts to 50g per liter olive oil produced [1].

For this specific region, the production of SNG would probably not be required due to the fact that the electricity is already being produced by means of diesel generators. However, in other olive oil production regions in Europe, heat and electricity are supplied from external sources or produced by means of other fuels like natural gas or LPG.

The results of the questionnaire elaborated by CNR showed that the energy required in the process is supplied also by means of other fuels apart from diesel. The results also show that the electricity is mostly supplied from external sources than produced on-site (see Figure 1, Figure 2 and Figure 3).

Figure 1: Bar chart of frequency of energy sources utilized (percentage of answered questions)

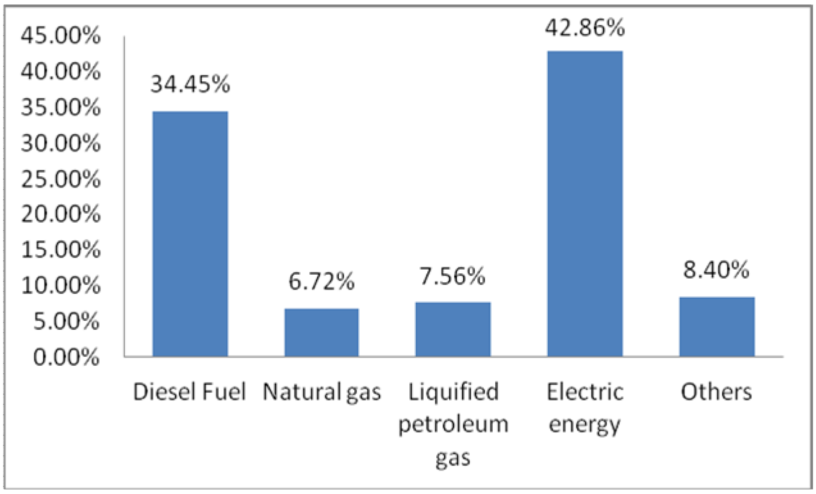


Figure 2: Bar chart of number of energy sources utilized by respondents (percentage of answered questions)

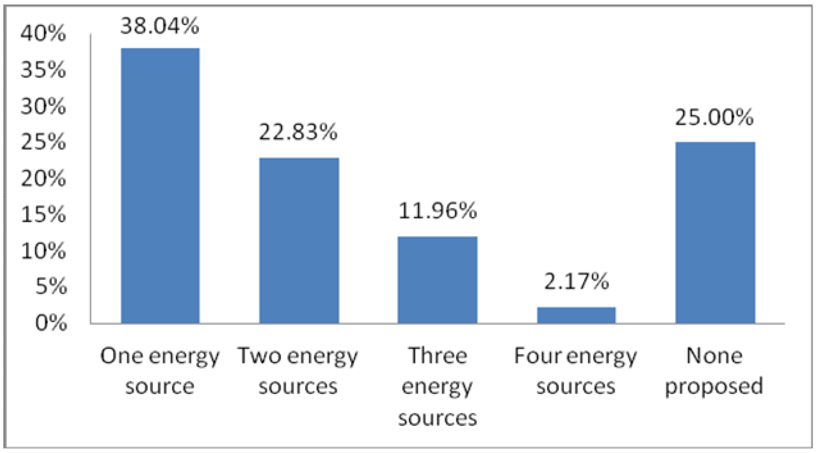
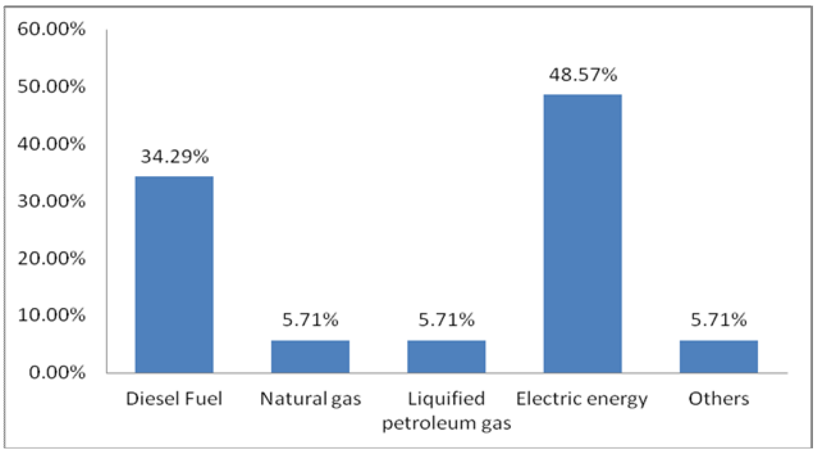


Figure 3: Bar chart of frequency of energy sources utilized by respondents who use only one energy source (percentage of answered questions)



2.2 Energy requirements in the drying of pomace and pomace oil extraction

The energy consumption data of this section is presented in Table 2:

Table 2: Energy inputs of the drying and pomace oil extraction processes per 1 kg of dry pomace (adapted from [2])

Input	Drying	Pomace oil extraction	Total	Units
Electricity	0.033	0.033	0.066	kWh/kg of dry pomace
Heat	0.074	0.179	0.253	kWh/kg of dry pomace

According to Intini [2], the production from olive oil industries in Italy, of oil and dry pomace was, respectively, 607021 and 1303136 tons in 2008. Therefore, the total energy required for this section could be estimated in 0.52 kWh per liter of olive oil produced (considering a density of oil of 0.85 kg/L [3]).

2.3 Total fuel and energy requirements. Required diesel/SNG ratio

Resuming the data presented in sections 2.1 and 2.2, the diesel, petrol and energy requirements to produce 1 L of olive oil are, respectively, 127 g, 50 g and 3.1 kWh.

In the case of using SNG to produce electricity, the amount of SNG to produce 1 liter olive oil, considering a gross calorific value of 43000 KJ/Nm^3 [4], and an efficiency of a combined cycle of 50% [5], would be of 0.52 Nm^3 for the study presented.

The required diesel/SNG ratio, or in other words, the consumption ratio between these two fuels in the process of olive oil production is 0.244 kg diesel/Nm^3 SNG.

On the other hand, the results obtained from the questionnaire elaborated by CNR showed a relation between required diesel and electricity of 18.6 g diesel/kWh electricity which differs from the one presented (40.9 g diesel/kWh electricity). This implies that the fuel and energy consumption of the study performed in this region of Cyprus is probably not fully representative. In any case, the literature study data will be used in the following section even though the diesel amount required could be overestimated. In the case of overproducing diesel, this diesel left could be either commercialized in the market or used for on-site electricity generation.

3 BTL/BTG carbon balance

The carbon atom in this section has been performed in basis of 1 L of olive oil produced in order to compare the amounts of diesel and SNG produced with the fuel requirements presented in section 2.3.

3.1 Biomass produced by olive cultivations

According to the information provided in the DOW of the FFW project, in Italy, the average yearly biomass produced by olive cultivations is 1.7 t/ha. In the other hand, the average production of olive oil per hectare in Italy during 2010 was 0.44 t/ha [6]. As a result, we can estimate that the biomass produced for every liter of olive oil manufactured is: 4.55 kg/L (considering a density of olive oil of 0.85 kg/L).

In order to convert this amount into carbon atoms it is necessary to know the carbon content of the different kinds of biomass present. According to Intini [2], 1.7 kg/L of the biomass produced correspond to de-oiled pomace residues. The rest of the biomass produced has been considered as woody biomass to calculate the carbon content. The carbon content of these two materials is presented in Table 3.

Table 3: Carbon content of the different types of biomass

Type of biomass	Carbon content (kg C/kg)	Reference
De-oiled pomace	0.481	[7]
Pruning residues/Wood	0.475	[8]

The resulting amount of carbon per liter of olive oil produced is: 2.17 kg of C.

3.2 Gasification

Before presenting the carbon product distribution in the gasification step it should be commented that, in order to increase the productivity of the different catalytic reactions after gasification, the oxidizing media for gasification should be pure oxygen, instead of air. Thereby, the partial pressure of the reactants in the different catalytic reactions will not be diminished by the presence of nitrogen.

The following product distribution presented in Table 4 has been used to calculate the amount of carbon useful for production of fuels. The data presented in Table 4 corresponds to a gasification with pure oxygen (99.5% O_2) in a circulating fluidized bed gasifier working at 850 ºC and 1.3 bar [9].

Table 4: Carbon atom selectivity in biomass gasification (adapted from [9])

Compound	Carbon atom selectivity (%)
CO	23
CO_2	40
CH_4	14

As a result from the gasification step, only 0.5 kg of C (which corresponds to 1.16 kg of CO) is useful for the synthesis of fuels. The carbon selectivity to CO of the gasification at these conditions is very low, however, the resulting H_2/CO ratio of the gasification is higher than usual: 1.64 [9]. Therefore, the overall carbon efficiency after the water gas shift reaction (in which part of CO is converted to CO_2) does not differ significantly from gasification processes leading to higher carbon selectivity to CO and lower H_2/CO ratio.

3.3 Water gas shift, Fischer-Tropsch and methanation

In this section, the results from section 2.3 (diesel and SNG consumption in the olive oil production) have been used to calculate the corresponding amounts of CO required and comparing these with the available amount of CO after the gasification step.

Fischer-Tropsch synthesis

The selectivity to the different products resulting from the FT synthesis is presented in Table 5. These correspond to experimental results obtained with a 12wt.%Co-0.5wt.%Pt/ɔ-Al_2O_3 catalyst prepared in KTH at industrial relevant conditions (210 ºC and 20 bars).

Table 5: FT product distribution

Product	kg product/kg CO
SNG	0.061
Ethene	0.015
Propene	0.015
LPG	0.018
C5-C10 (~naphtha/petrol)	0.113
C11-C21 (~diesel fraction)	0.189
C22+ (FT waxes)	0.085

According to Leckel [10], the mass yield of diesel produced from hydrocracking LTFT waxes at high conversions is around 65%. The mass yield of naphtha is around 21%. In Table 6, the final product distribution of SNG, naphtha and diesel are presented having in consideration the hydrocracking products.

Table 6: Product distribution after Hydrocracking of FT waxes

Product	kg product/kg CO
SNG	0.061
C5-C10 (~naphtha/petrol)	0.131
C11-C21 (~diesel fraction)	0.244

The results from section 2.3 showed that the amount of diesel required for producing 1 L olive oil is 0.127 kg. According to Table 6, in order to produce this amount of diesel, 0.52 kg of CO are needed.

The water gas shift reaction ($CO+H_2O \rightarrow CO_2 + H_2$) decreases the amount of CO available for the fuel synthesis. The H_2/CO ratio needed for LTFT is 2.1, and that the H2/CO ratio resulting from gasification is 1.64. Therefore the required amount of CO in order to produce 0.127 kg of diesel is 0.61 kg. This amount has simply been calculated by means of the stoichiometry of the WGS reaction.

The naphtha produced from this amount of CO is 68 g which covers the demand of petrol (50 g) showed in section 2.3.

<u>Methanation</u>

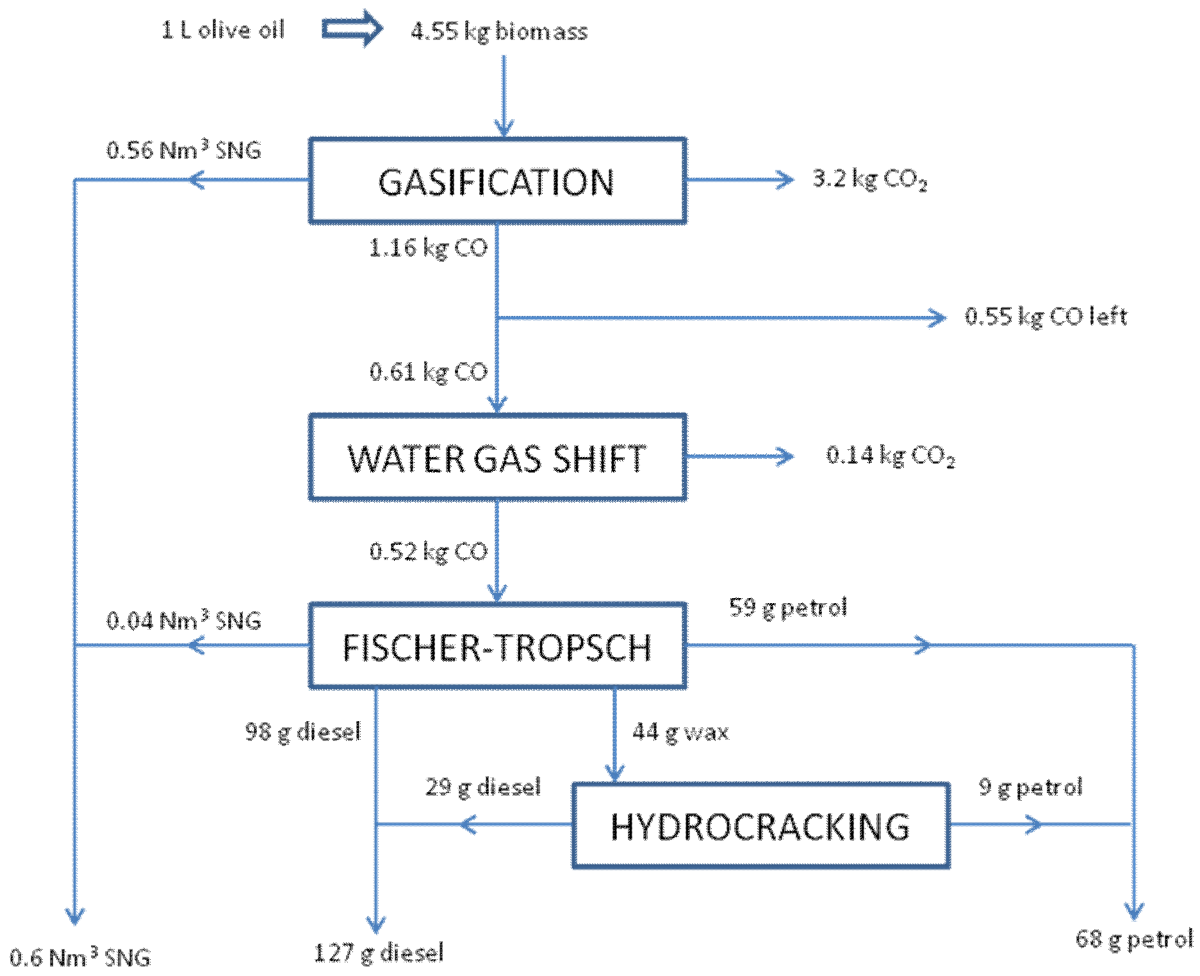
The amount of SNG produced in the gasification and Fischer Tropsch steps, so only by means of the BTL process, is 0.6 Nm^3, which already covers the SNG demand for electricity and heat in the olive oil production process.

Therefore, 0.55 kg of CO are left from the gasification process, which can be used to produce either diesel or SNG.

3.4 Scheme of the carbon balance

In order to clarify and summarize the calculations presented in the previous sections a block diagram with the amounts of the different carbon-based components is presented (see Figure 4).

Figure 4: Block diagram of the BTL carbon balance



4 Definition of the diesel/SNG ratio

4.1 Definition of the FT and methanation production

The result of this study showed that the amount of biomass produced by olive cultivations is enough to cover the energy demands of the olive oil industry. In section 3, it was showed that approximately 0.55 kg of CO per liter of olive oil produced are left from the gasification step.

It should be convenient to state that, the FT synthesis, in comparison with methanation, requires an additional catalytic reaction step (hydrocracking) and produces a range of undesired products, implying separation processes.

Moreover, the heat released from the methanation reaction can be recovered as high pressure super heated steam to be used directly in a steam turbine and increase the overall energy efficiency of the process [11].

In KTH, we suggest to use this amount of CO left from the gasification step to produce SNG. Our recommendation is to apply the concept of integrated co-production of SNG and diesel which results in a higher biomass-to-fuel efficiency [12]. The SNG produced would not only be used to cover the electricity and heat demands of the olive oil production but also the energy requirements of different FFW process steps (pumps, compressors, fuel separation processes, air separation unit...).

This decision concerning the usage of the CO left was discussed and approved in a round table with all the FFW partners in the 6-month meeting in Madrid.

In conclusion, the final diesel/SNG ratio considering this option would be 0.142 kg diesel/Nm^3 SNG.

4.2 Price and consumption of diesel and natural gas in the market

The possibility of commercializing these fuels in the market and the benefit that would be taken from it, could also affect in the diesel/SNG production ratio. Unfortunately, the FFW process is not designed yet, and it could be very inaccurate to estimate the production cost of these two fuels.

The purpose of this section is to provide part of the information necessary to calculate the benefit of the production of these two fuels. This could be of special interest in the definition of the most profitable diesel/SNG ratio once the FFW demo plant is built.

This information is only presented for the European countries with highest production of olive oil which, according to the information provided in the DOW Part B (Page 3 Figure 3) are Spain, Italy and Greece.

4.2.1 *Consumption of diesel and natural gas*

The source of information in this section has been taken from IEA (International Energy Agency). The following table corresponds to the domestic supply during 2009, which considers both the final consumption and the transformation of these fuels into electricity and heat.

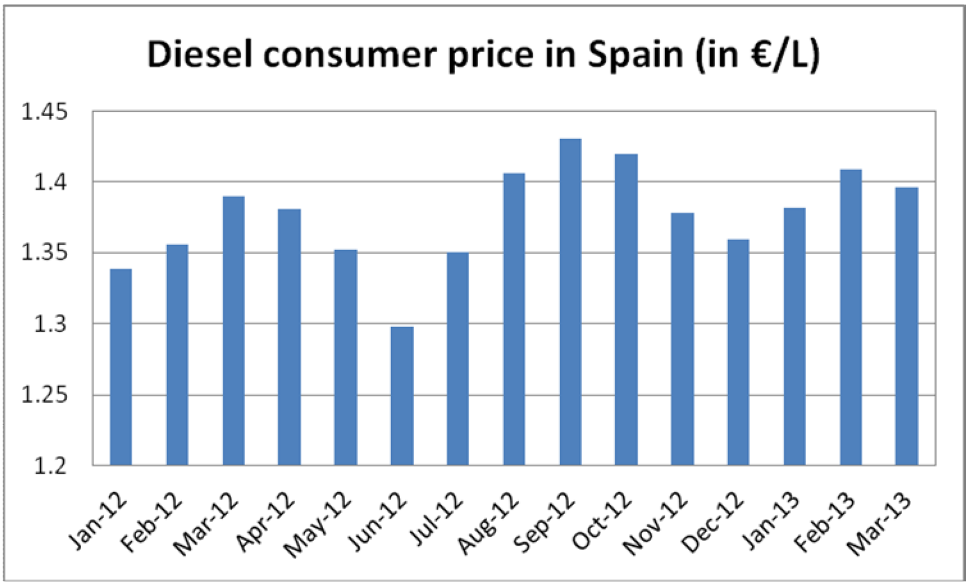
Table 7: Domestic supply 2009 (adapted from IEA [13])

Fuel	Spain	Italy	Greece	Units
Diesel	31361	28943	6597	1000 tones
SNG	1452447	2972717	138211	TJ (GCV basis)

4.2.2 *Price of diesel and natural gas*

Below, the diesel and natural gas prices in Spain, Italy and Greece are presented.

Figure 5: Diesel consumer price in Spain (adapted from [14])



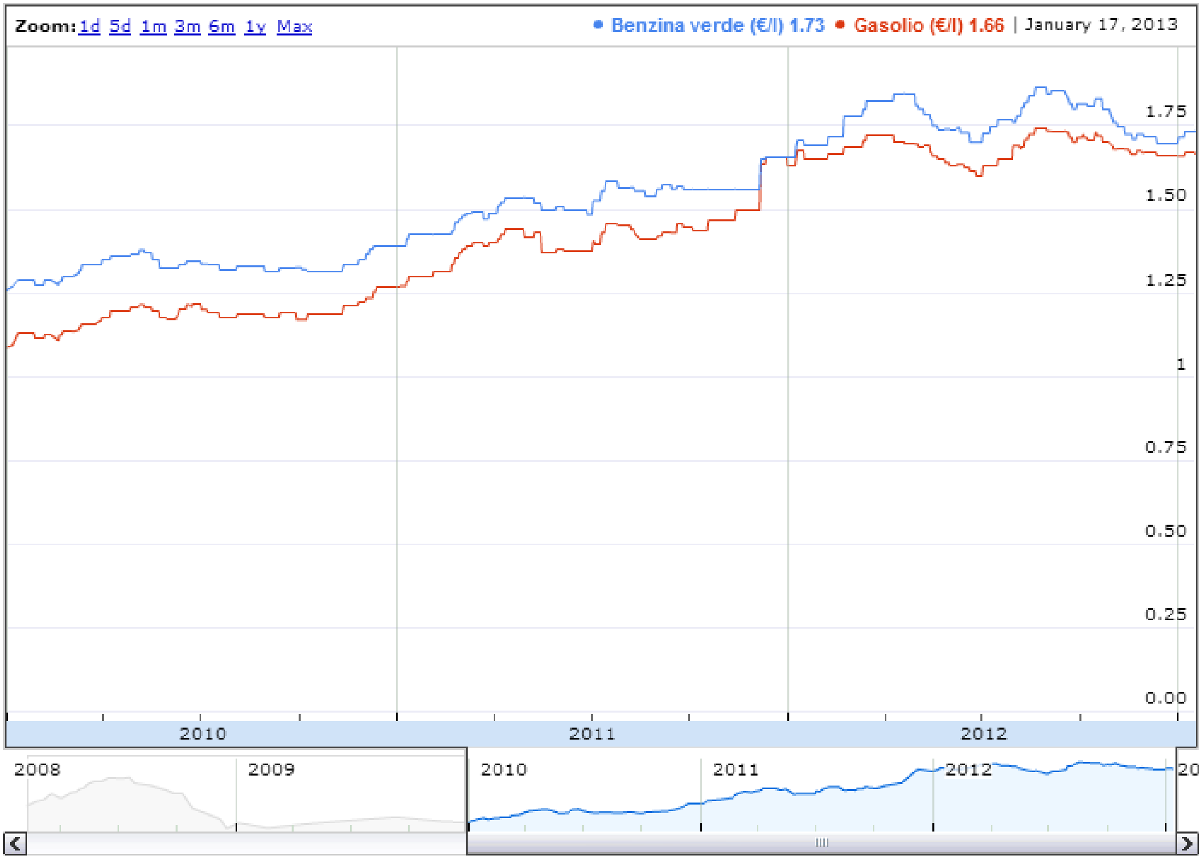
Tendency=+0.042 ú/year (calculated from January 2012)

Price Diesel (2012-03-11) = 1.390 ú/L [15]

Table 8: Natural gas price in Spain in ú/kWh (adapted from [15])

Households			Industry		
2010	2011	2012	2010	2011	2012
0.053	0.054	0.054	0.028	0.029	0.029

Figure 6: Diesel consumer price in Italy [16]



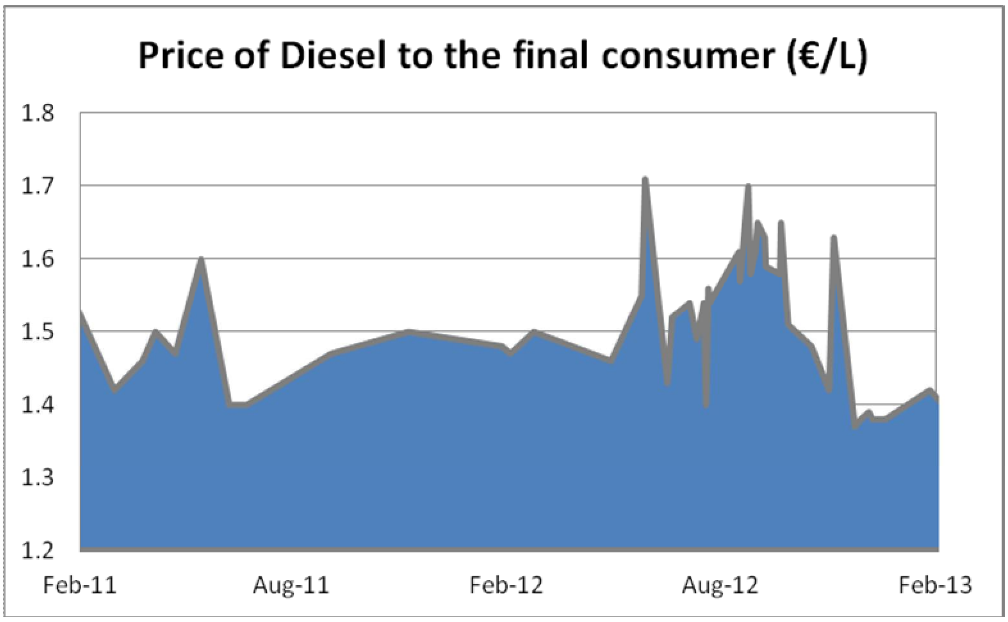
Tendency=+0.016 ú/year (calculated from January 2012)

Price Diesel (2012-03-11) = 1.752 ú/L [15]

Table 9: Natural gas price in Italy in ú/kWh (adapted from [15])

Households			Industry		
2010	2011	2012	2010	2011	2012
0.062	0.069	0.069	0.030	0.031	0.031

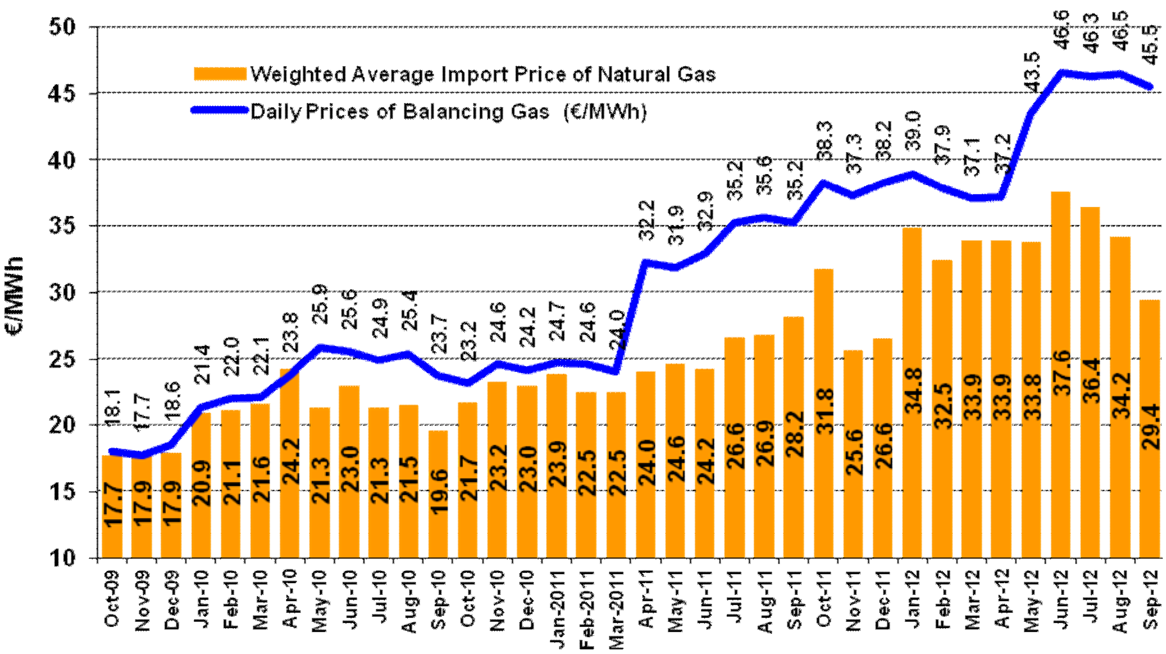
Figure 7: Diesel consumer prince in Greece (adapted from [17])



No increasing tendency

Price Diesel (2012-03-11) = 1.435 ú/L [15]

Figure 8: Natural gas price in Greece [18]



5 Conclusions

The fuel and energy requirements of the production of olive oil have been estimated in 127g of diesel, 50g of petrol and 3.1 kWh of electricity and heat per liter of olive oil produced. The amount of SNG necessary to produce 3.1 kWh is approximately 0.52 Nm^3.

The amount of biomass produced from olive cultivations is enough to cover the fuel and energy requirements of the olive oil production process. The amount of SNG produced by means of the FT synthesis and gasification is already higher than 0.52 Nm^3.

The decisions regarding the production of electricity by means of SNG and the production of SNG using the surplus of CO were discussed and approved by all the FFW partners in a round table.

The resulting diesel/SNG production ratio of the study is: 0.142 kg diesel/Nm^3 SNG.

6 Attachment 1

DELIVERABLE REVIEW REPORT

Reviewer	
Date	
Reviewed Deliverable	

1. Technical result of the deliverable

Deliverable covers the topic specified in the title					
Yes		Partly		No	

Technical contents are relevant to Trans-IND and to the covered WP					
Yes		Partly		No	

Presented results in the deliverable are of high value					
Yes		Partly		No	

Technically sound of the deliverable					
Sound and flawless		Seems OK		No, it has problems	

Described work in the deliverable follows a clear methodology

Sound and flawless		Seems OK		No, it has problems	

Please add your comments on the content and the technical results of the deliverable! Please comment the problems, if any!

2. Length, structure and presentation of the deliverable

Adequate length of the deliverable					
Yes, adequate		No, too long		No, too short	

Deliverable organization is appropriate					
Good		Fair		Restructuring needed	

Presentation of the deliverable clear and concise							
Very Good		Good		Fair		Rewrite	

Please add your comments on the length, the structure and the presentation!

7 References

[1] M. Avraamides and D. Fatta *Journal of Cleaner Production* **16** (2008)

[2] Intini F. *Journal of Sustainable Energy & Environment* **2** (2011)

[3] SIMETRIC, Available from: http://www.simetric.co.uk/si_liquids.htm.

[4] The Engineering ToolBox, Available from: http://www.engineeringtoolbox.com/.

[5] NaturalGas.org, Available from: http://www.naturalgas.org/.

[6] European Commission *Economic analysis of the olive sector* (2012) Report

[7] S. Camposeo and G.A. Vivaldi *Scientia Horticulturae* **129** (2011)

[8] National Forest Assessments, Available from: http://www.fao.org/forestry/17111/en/.

[9] C.N. Hamelinck, et al. *Energy* **29** (2004)

[10] D. Leckel *Industrial and Engineering Chemistry Research* **46** (2007)

[11] Haldor Topsoe *From solid fuels to substitute natural gas (SNG) using TREMPÊ* Catalog

[12] R.W.R. Zwart and H. Boerrigter *Energy and Fuels* **19** (2005)

[13] International Energy Agency, Available from: http://www.iea.org/.

[14] DieseloGasolina.com, Available from: http://www.dieselogasolina.com/Estadisticas/Historico.

[15] Europe's Energy Portal, Available from: http://www.energy.eu/.

[16] Unico-lab, Available from: http://unico-lab.blogspot.se/2010/01/archivio-storico-prezzi-benzina-e.html.

[17] Gasoline-germany.com, Available from: http://gasoline-germany.com/international.phtml?kontinent=EU&land=63&waehrung=EUR&einheit=Liter.

[18] PAE-RAE, Available from: http://www.rae.gr/site/el_GR/categories_new/about_rae/factsheets/general/07122012_1.csp.